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Spectroscopic Studies of the Hydrogen Bond. II. The Shift of the O-H Vibrational Frequency in the Formation of the Hydrogen Bond*

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The association spectra of a number of acids and alcohols in the region λλ9000–11,000 have been observed both in solution and in the pure liquids. In each case a broad band with maximum near λ10,000 was observed while in the alcohols an additional weaker band near λ9000 appears to be present. Evidence is presented that the λ10,000 band is to be identified with the O−H group. This evidence includes the behavior of the association band with change in concentration and temperature and its presence in several substances in which absorption other than that due to the O−H group is practically absent in the region studied. New evidence is given that a weak intermolecular hydrogen bond is formed between acetone and methyl alcohol. It is pointed out that the presence of absorption in the narrow O−H bands is not to be taken as evidence of the absence of hydrogen bonds in case the absorption is weak. The character of the O−H absorption in the case of intermolecular hydrogen bonds is discussed and the probable nature of the spectrum in the case of an intramolecular bond is indicated. A relation between the energy of the hydrogen bond and the shift of the O−H vibrational frequency is pointed out and its use is suggested in the interpretation of certain spectra.

INTRODUCTION

RECENTLY there has been considerable interest shown in a peculiar form of linkage sometimes known as the "hydrogen bond" in which a hydrogen atom, usually belonging to an hydroxyl or amino group, appears to serve as a connecting bridge between two electronegative atoms. The concept of the hydrogen bond has been most useful in the explanation of many cases of molecular association as well as of the closing of rings within a molecule. It has served in the interpretation of many facts which have come to light in the course of physico-chemical investigations of the ordinary sort, and in other fields has been able to account for numerous results which at first sight would appear to be rather anomalous. These include certain dipole moments and some internuclear distances, determined by x-ray and electron diffraction measurements, which would be expected to be much larger in the absence of some such bond.[1] Though investigations of the types mentioned appear to have established the existence of some peculiar form of bond and have given information about the conditions under which it is to be expected, and in very few cases an estimate of its energy, there are certain points on which they seem to be incapable of giving information. Indeed the exact nature of the bond is not yet clear and it has not been shown in what way the hydrogen atom is involved.[2]

* This investigation is a part of a program of research made possible by a grant-in-aid from the National Research Council to one of us (R. M. B.) for which it is desired to express appreciation.

[1] For references, see M. L. Huggins, J. Org. Chem. 1, 407 (1936).

[2] It has not been shown, for example, that the hydrogen atom lies on a line connecting the two atoms which it appears to join, though this is often assumed.

It has recently become evident that spectroscopic investigations are particularly suitable for clarifying a number of doubtful points, since they do give rather direct information about the condition of the hydrogen atom and the strength of its attachment to the atoms with which it is connected. A number of facts have been made evident but no very systematic interpretation has so far been made of the spectroscopic evidence already available which at the moment presents a somewhat confused picture.

Among the facts known are the following. In a considerable number of compounds containing hydroxyl hydrogen, which for various reasons is supposed to be tied up in a hydrogen bond, O−H bands of the approximate frequency and general narrow character of those found in the vapors or dilute CCl_4 solutions of the simple alcohols are absent from the infrared absorption spectrum. Absence of absorption in the 3600, 7100, or 10,400 cm^{-1} regions has consequently come to be accepted as a spectroscopic criterion for the presence of a hydrogen bond.[3, 4] That this is justified we have demonstrated in a previous paper[5] in which we showed that in acetic acid vapor the intensity of the sharp O−H bands at 10,240 cm^{-1} is a quantitative measure of the concentration of single molecules and consequently of the number of hydroxyl groups not involved in those relatively strong hydrogen bonds which appear to be responsible for association.

However, in a number of cases in which intramolecular bonds might perhaps have been possible Hilbert, Wulf, Hendricks and Liddel report an absorption band near 7100 cm^{-1}, though it is sometimes rather weak and often accompanied by subsidiary bands on the low frequency side. These workers apparently take any absorption at 7100 cm^{-1} as indicative of the absence of hydrogen bonds.

The absence of normal O−H absorption may be taken as evidence of considerable modification of the hydroxyl group on hydrogen bond formation. How great this is in the intramolecular

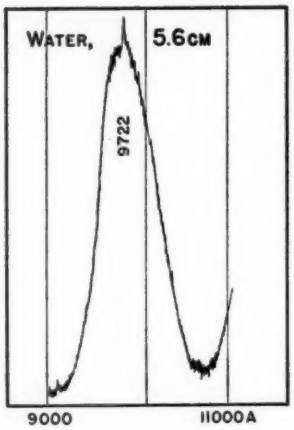

FIG. 1. The absorption band in liquid water at λ9722.

bonds has not been made clear since when the 7100 cm^{-1} bands were absent the workers mentioned above did not report whether or not there were other bands on the low frequency side which could be identified with a shifted O−H frequency.[6] This question is of fundamental importance since in some views of the hydrogen bond it has been regarded that the modification of the O−H, or N−H group may be so great that one could no longer speak of an O−H, or N−H frequency.

In numerous cases of intermolecular hydrogen bonds in associated molecules, or in crystals, absorption bands are present which must be identified with an O−H vibration. In water for example, of which one band is reproduced in Fig. 1, there is no other frequency which could be responsible. It appears not always to have been realized that these bands are decidedly different in appearance from those characteristic of the hydroxyl group in the alcohol vapors, for example, though they are indeed much broader and considerably shifted to lower frequencies. This frequency shift is evidence of a material modification of the O−H group but still not enough to destroy its identity or greatly alter its force constant or internuclear distance.

Numerous studies have been made of the spectra of binary liquid mixtures[7] in an attempt

[3] Hilbert, Wulf, Hendricks and Liddel, J. Am. Chem. Soc. **58**, 548 (1936).

[4] In this paper we shall confine ourselves almost exclusively to the O–H–O linkage but similar investigations have been made of other types of bridge. See M. Freyman and M. R. Freyman, J. de phys. et rad. **7**, 506 (1936).

[5] Badger and Bauer, J. Chem. Phys. **5**, 605 (1937).

[6] In one case of the intramolecular bond a shifted O-H band has been observed in the 3μ region. It has been shown that in *o*-nitrophenol the hydroxyl group is responsible for a considerable part of the absorption near 3300 cm^{-1}. See Buswell, Deitz and Rodebush, J. Chem. Phys. **5**, 501 (1937).

[7] See Williams and Gordy, J. Am. Chem. Soc. **59**, 817 (1937). This paper contains references to previous work.

to demonstrate the formation of hydrogen bonds between dissimilar molecules. In a number of cases the spectrum of a mixture, such as of alcohol and acetone,[8] was found to differ appreciably from the calculated sum of those of the components. The reported shift of the C—O frequency of acetone on mixing with alcohol is very interesting if real. Unfortunately such comparisons of observed spectra with those calculated from Beer's law are likely to be considerably in error unless the observations are made with extreme precision and great resolving power. It would be more convincing if a comparison were made between the spectrum of the mixture and that obtained when the separate components were placed in two absorption cells in series in the absorption path.

The observations on the O—H frequency might at first sight seem to indicate the opposite of that which was intended. In liquid alcohol the hydroxyl hydrogens are presumably almost entirely engaged in hydrogen bonds, and the apparent shift of the O—H band to higher frequencies on dilution with acetone shows that these bonds are broken by a decrease in association and if any new ones are formed between the dissimilar molecules they must be relatively weak. It is evident that additional facts are needed in order to make a satisfactory interpretation of the data on liquid mixtures.

There are numerous gaps in our knowledge which must be filled before we can fully understand what spectroscopy is able to tell about the condition of the O—H or N—H groups involved in hydrogen bonds. There still seems to be some doubt as to whether there may be different kinds of these bonds which may be distinguished in type as well as degree, in particular whether or not there is any essential difference between the intermolecular and intramolecular bonds.

We have consequently undertaken a study of the O—H absorption under a variety of conditions chosen so as to answer some of these questions. This is a very favorable case for investigation since, owing to the fact that the angle between the two oxygen bonds is not greatly different from 90°, the valence frequency of the O—H group is but little affected by differences of mass in the molecules to which it is attached though it is greatly altered by interaction of the O—H group with other atoms in its immediate environment. We have previously observed small shifts in the O—H frequency in going from the primary to the secondary and tertiary alcohols and much larger ones in going to the unassociated oxy-acid molecules.[9] In this paper we shall consider some cases in which the O—H group has been considerably modified by entering into a hydrogen bond and shall show what kind of spectrum is generally to be expected in this case.

Experimental

The greater part of the investigation was carried out with the use of a large Littrow glass spectrograph with a dispersion of about 70A per mm at λ9000, though a few exposures were made with higher dispersion to settle some doubtful points. Eastman 1Z plates, sensitized with ammonia, were used throughout. Two different preparations of these plates were used. The earlier one, with which most of the work was done, showed very uniform sensitivity over a wide range, though there was a maximum near λ10500 and the sensitivity dropped off very rapidly beyond λ11,000, as may be seen in the last section of Fig. 2. The broken curves represent the background blackening at a number of different intensities and were obtained by interposing screens with the transmissivities indicated in the diagram. We have had some difficulty in carrying out any precise photometry with ammonia sensitized plates, but most of the microphotometer curves may be at least qualitatively interpreted by use of the curves of Fig. 2. The second preparation of 1Z plates showed a somewhat different sensitivity curve and had a more pronounced maximum near λ10500. Spectra taken with the second emulsion are shown in Figs. 3, 4, 5, and the last section of Fig. 7.

The wave-lengths of most maxima, as well as of some points of inflexion in the curves which are definitely real, are indicated in the diagrams. It is difficult to measure accurately the maxima of broad bands in regions where the plate

[8] W. Gordy, Phys. Rev. **50**, 1151 (1936).

[9] Badger and Bauer, J. Chem. Phys. **4**, 711 (1936).

sensitivity shows a trend, but we do not believe that the errors are great.

In regard to the materials used it does not seem necessary to make any remarks other than that adequate precautions were taken to secure purity. In the investigation of sulfuric acid the fuming acid was used. The phosphoric acid was prepared by adding P_2O_5 to 90 percent acid to make up to the formula H_3PO_4.

Discussion of the Results

In beginning this investigation we were confronted by one difficulty in particular. In searching for bands which may be ascribed to the vibrations of a somewhat modified O—H group, the frequency of which is not precisely known, it is frequently difficult to make a positive identification owing to the possible presence of bands of other origin in the same region. We soon found that in many cases of intermolecular hydrogen bond formation not only is the hydroxyl frequency considerably decreased but the characteristic bands are greatly broadened so that the intensity of absorption at any point is relatively small. Rather great path lengths are required for their study which in organic compounds frequently bring out various weak bands involving C—H and other vibrations. These could easily escape attention under the conditions suitable for observing the normal narrow O—H bands, but are sometimes bothersome in the study of the broad bands. The most certain identification can of course be made when the same substance can be studied both when the O—H group is relatively unperturbed and when it is involved in a hydrogen bond, with other conditions being kept similar and *with the same amount of material in the absorption path* in the two cases. With the alcohols this was possible but with most other substances it was not and we were obliged to use evidence which is somewhat indirect. We have studied several substances in which the region of spectrum under observation must be practically free from any bands not concerning the O—H vibrations, and have compared them with others in which this may not be the case and so have been able to come to rather definite conclusions.

The Alcohols

A very favorable situation is found in the alcohols since they can be studied at various concentrations in a more or less inert solvent such as CS_2 or CCl_4 and the changes in spectrum as association progresses with increase in concentration are easily followed. There seems little doubt that the association which has been demonstrated by freezing point measurements, for example, is due to hydrogen bond formation. One may make an estimate of the energy of the bond in two different ways which agree very well and are probably not much in error. By comparing the heats of vaporization of the alcohols with those of the paraffins, or by plotting the former against the number of carbon atoms and extrapolating to zero, one concludes that the O—H group contributes about 7500 cals to the energy of vaporization of the lower primary alcohols. The greater part of this energy may be attributed to the hydrogen bond since a more accurate determination in the case of acetic and formic acids gave practically the same value per bond for the dissociation energies of the double molecules.

The characteristic "association bands" which replace the sharp O—H bands at high concentrations of the alcohols have been observed by several workers.[10-12] We have studied them in detail in CH_3OH through a wide range of concentration keeping the amount of alcohol in the absorption path and the temperature constant. As will be seen in Fig. 2 there are two absorption regions which may definitely be designated as association bands. The more intense one is on the low frequency side of the O—H band of the monomer and has a maximum around $\lambda 10{,}000$; the other, on the high frequency side, is relatively narrow and weak but seems to be quite real. (The fourth harmonic of the C—H frequencies is located in about this region but can only be responsible for a small part of this band since the intensity increases with concentration.) Both bands show some structure which is much more evident in the original plates than in the microphotometer curves. The shoulders on the curves

[10] Errera and Mollett, Nature **138**, 882 (1936).
[11] Fox and Martin, Nature **139**, 507 (1937).
[12] Kinsey and Ellis, J. Chem. Phys. **5**, 399 (1937).

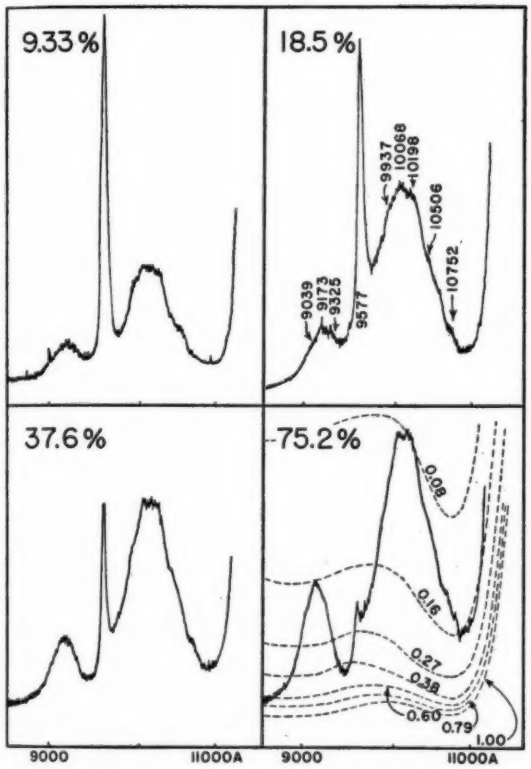

FIG. 2. The absorption spectrum of methyl alcohol in carbon tetrachloride solutions. The concentrations are in mole percent and the path lengths were inversely proportional to the concentration so that the amount of alcohol in the path was constant. The broken curves in the last diagram represent the background blackening with only carbon tetrachloride in the cell and with screens of the transmissivities indicated interposed in the path.

which are designated with wave-lengths are definitely real.

Though the origin of the high frequency association band may be in some doubt we have no hesitation in ascribing the broader and more intense one to a shifted O—H vibration. The behavior of the band on change of temperature is very convincing, as will be shown later. We have made a comparison of the integral molecular absorption coefficient of the narrow O—H band in the state of complete dissociation with the sum of those of the two bands in the associated molecule and find that the latter is certainly not smaller but probably considerably larger. There are difficulties in the way of comparing very narrow with very broad bands but we believe our accuracy is sufficient to show that the total O—H absorption does not decrease greatly on association.

It is of particular interest that the entire association spectrum appears to develop simultaneously and at about the same rate as the concentration is increased. This is quite different from the situation found by Errera and Mollet[10] in their temperature studies of the O—H bands in ethyl alcohol.

Broad association bands with maxima around λ10,000 are found also in the spectra of several higher alcohols which we have investigated. Examples are shown in Figs. 3 and 6. The situation on the high frequency side of the sharp O—H bands is more difficult to interpret owing to the presence of the fourth harmonic band of the C—H frequencies. This is evidently very weak in methanol, in ethanol it is quite evident at λ9098, and in the higher alcohols becomes quite intense. In ethanol a weak high frequency association band appears at about λ9400, distinct from the C—H band, but in the heavier compounds it is entirely obscured, if present. Some observations on temperature effects which will be described below indicate that it is indeed present, superposed on the C—H harmonic.

In the aromatic compounds the situation is very unfavorable since even in the λ10,000 region there are bands of appreciable intensity which do not involve the O—H vibration, but presumably result from combinations of the C—H and double bond C=C vibrations.

In the lower primary alcohols the sharp O—H bands are practically absent from the spectra of the liquids, but as the number of carbon atoms increases they show up with appreciable intensity. Note for example *n*-amyl alcohol shown in Fig. 3. This fact need not be ascribed to a weaker hydrogen bond but may well be due to the greater entropy change on dissociation.

In comparing normal, secondary and tertiary alcohols in the liquid state one finds that the intensity of the sharp O—H bands increases in the order given, as shown in Fig. 3, which duplicates observations made by Naherniac[13] except as regards the wave-lengths of the maxima. These differences may be correlated with data on heats of vaporization. For example the heats of vaporization of *n*-propyl and isobutyl alcohols are greater than those of isopropyl and tertiary-butyl alcohols by about 300 and 500 cal., respec-

[13] A. Naherniac, Ann. de physique **8**, 528 (1937).

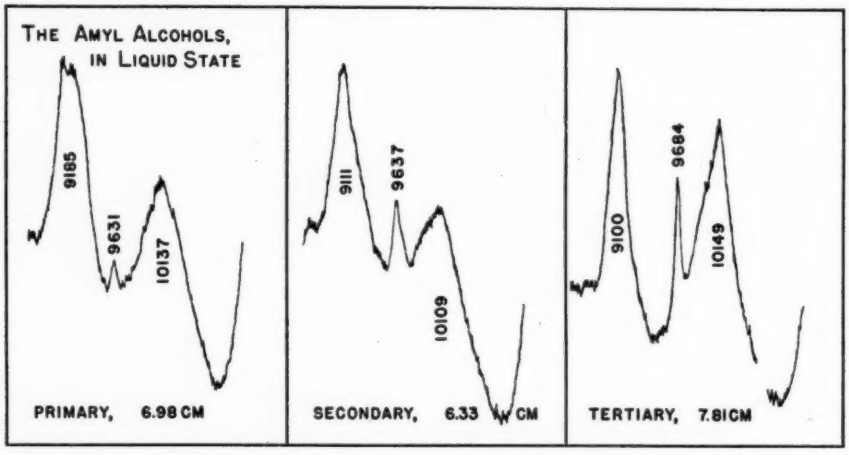

FIG. 3. Comparison of the spectra of the liquid amyl alcohols showing the increase in intensity of the narrow O–H band in going to the secondary and tertiary compounds.

tively. Although these facts point to slightly weaker hydrogen bonds, we are inclined to attribute this entirely to steric factors, namely the crowding of CH_2 or CH_3 groups around the hydroxyl radical which prevents the close approach of two oxygen atoms, since in mixtures of methanol with a secondary or tertiary alcohol the sharp O−H bands disappear. See Fig. 4.

EFFECT OF TEMPERATURE ON THE ASSOCIATION BANDS

Errera and Mollet have studied the effect of temperature on the spectrum of a solution of ethyl alcohol in CCl_4,[10] but the results are not simple to interpret. It seems clear that not only a change in the degree of association but also an actual alteration of the spectra of the associated molecules are involved. It is indeed difficult to separate these two effects but it seemed worth while to investigate the temperature changes in the spectra of some of the lower alcohols which in the liquid condition show little absorption in the sharp O−H bands even up to 75°C, and can in a sense be regarded as nearly completely associated.

The spectra of liquid methyl, ethyl and *tert*-amyl alcohol all showed certain changes in common as the temperature was raised. Microphotometer curves of the first two are shown in Fig. 5. In each case absorption decreased in the vicinity of λ9000 but increased markedly in the region between the position of the O−H band of the monomer and the maximum of the λ10,000 association band. In methyl alcohol no trace of a sharp O−H band is evident even at 71°, but at the point where it should be expected the long wave association band shows a very sharp edge. At higher temperatures the narrow band becomes quite evident in ethyl alcohol and moderately strong in *tert*-amyl alcohol in which it is present even at 1°C. In each case as the temperature is raised there is a noticeable shift of the maximum of the λ10,000 association band to shorter wave-lengths, but it is most evident in methyl alcohol.

As mentioned above, it seems evident that in the λ9000 region there is superimposed on the fourth harmonic of the C−H frequency another band which is intimately connected with association. One should not expect the C−H band to be much affected by temperature or association but the λ9173 band of methanol is very dependent on both. In this substance the C−H band should be in any case relatively weak. In ethanol two separate bands are evident. The more intense one of shorter wave-length seems little altered by temperature though the other is considerably affected. In *tert*-amyl alcohol the strong and apparently single band in this region must be due in large part to the C−H harmonic but there is nevertheless a considerable decrease in intensity with temperature.

The Simple Organic Acids and Some Inorganic Oxy-Acids

In the case of the acids we did not find it possible in the λ10,000 region to follow the course of the spectrum from the state of complete dissociation to that found in the double molecules. We have been able to follow the weakening in intensity of the sharp O−H band at λ9760 in acetic acid vapor as association proceeds,[5] but the greatest path length which it was convenient to use, though well adapted to the study of the bands in the monomer in which the intensity is concentrated in a narrow region, was not sufficient to make evident any trace of an association spectrum. In solutions of the acids association is practically complete even at the highest temperature which one can use without an apparatus designed for high pressures.

In CCl_4 solutions of a number of monobasic organic acids we have observed broad bands in the λ10,000 region, some of which are shown in Fig. 6. They are very similar to the association bands of the alcohols and it seems reasonable to attribute them in part at least to a shifted O−H frequency. However, to make the situation clearer we have investigated a number of substances in which the O−H vibration is the only one of high frequency and in which the λ10,000 region should be free of any bands of appreciable intensity for which it is not responsible. These substances include trichlor-acetic acid, fuming sulfuric acid and phosphoric acid, all of which one should expect to be largely or completely associated by hydrogen bonds. In each case we have observed broad bands similar to those of the organic acids, though there are differences in the distribution of absorption and in the position of the maxima.

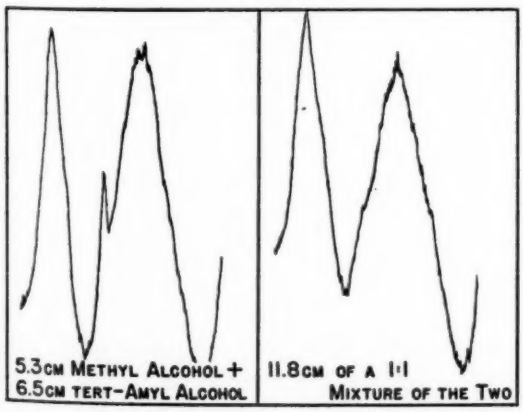

FIG. 4. The disappearance of the narrow O–H band of *tert*-amyl alcohol on addition of methyl alcohol. The spectrum in the first diagram was obtained with the two alcohols in separate cells in series in the light path.

Hydrogen Bonds Between Unlike Molecules

We have devised one experiment to see whether the existence of hydrogen bonds between unlike molecules could be demonstrated spectroscopically in a much more direct way than by the studies of liquid mixtures which were mentioned above, and to provide additional information for interpreting those experiments. We have compared the spectra of CCl_4 solutions of methyl alcohol, of acetone, and of the two together. The alcohol solutions were sufficiently dilute that dissociation was great though not complete. On the addition of acetone the narrow O−H band decreased in intensity considerably, as shown in Fig. 7, which demonstrates rather directly the formation of a bridge between the hydroxyl and keto oxygens of the respective molecules. This is a very interesting case since it appears to be one in which resonance is unlikely though it is sometimes supposed to be essential in hydrogen bond formation.

The bond in question seems to be rather weak,

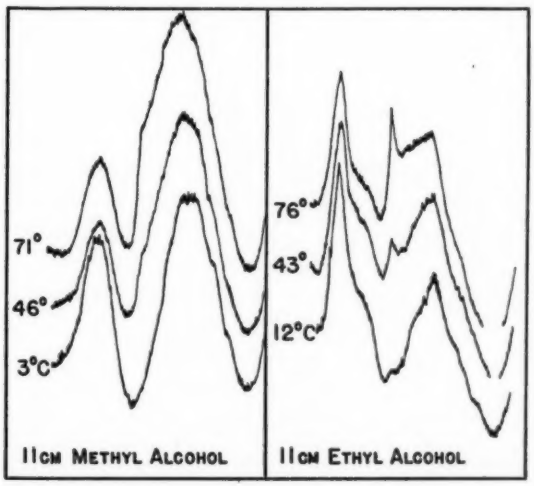

FIG. 5. Temperature dependence of the spectra of liquid methyl and ethyl alcohols. Origins of successive curves are displaced.

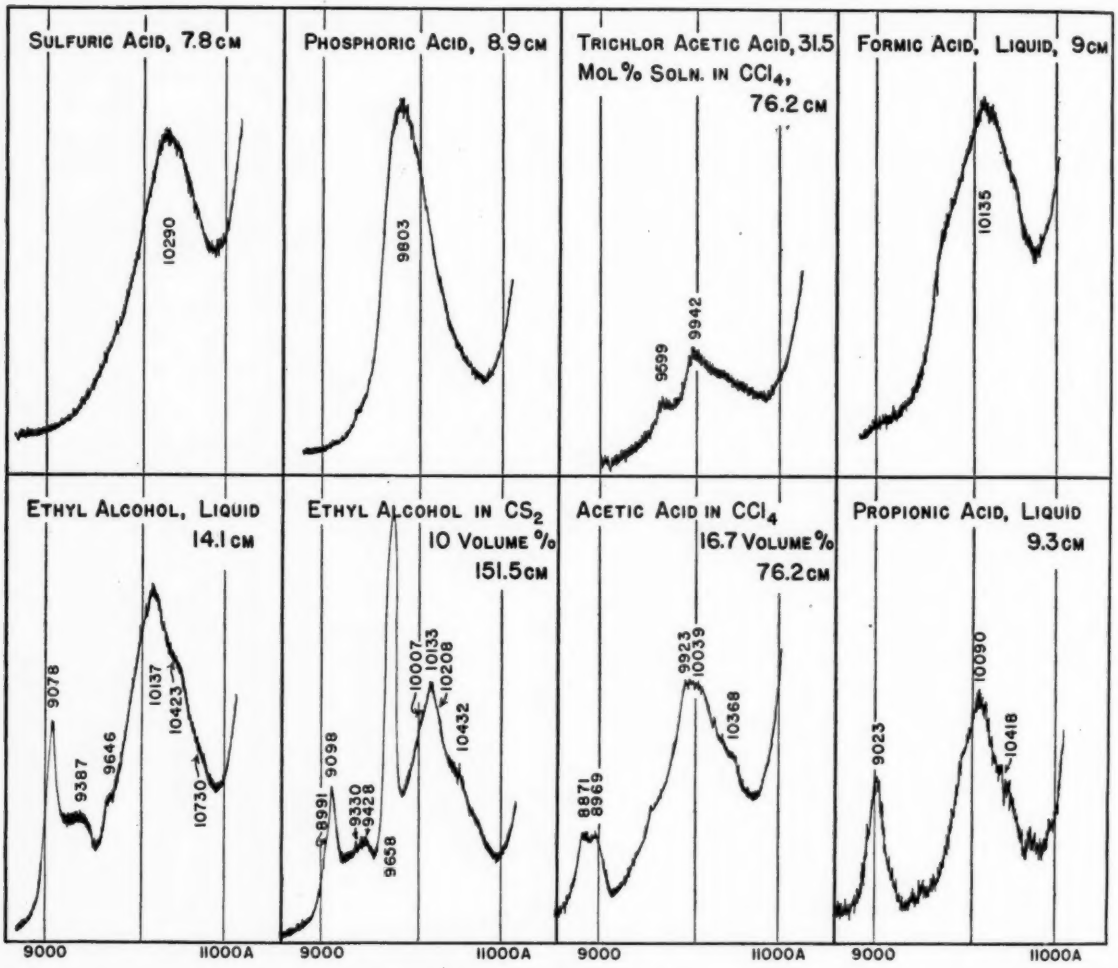

FIG. 6. Association bands in a number of substances. In the upper diagrams the bands must be attributed almost exclusively to a shifted O–H frequency. In the lower diagrams the weaker bands near λ9000 are due in part to the fourth harmonic of the C–H vibration.

however, as is indicated by the nature of the association spectrum. This is somewhat difficult to observe in all details since acetone itself has a strong absorption near λ10,000, due presumably to a combination of C−H and C=O vibrations; but the essential facts are clear and are especially evident in the spectrum of a solution of methanol in acetone shown in the last diagram of Fig. 7. No sharp O−H band is present such as would be observed in a solution of the same concentration in CCl_4, but continuous absorption sets in abruptly just at the point where this band would occur and comes to a maximum at considerably shorter wave-lengths than the center of the methanol association band.

The Intramolecular Bond Which May be Broken by Rotation of Some Group About a Single Bond

Hilbert, Wulf, Hendricks, and Liddel[3] have reported several cases in which an intramolecular bond might perhaps have been expected but was considered to be absent owing to the presence of a band near 7100 cm^{-1}, though this was sometimes weak. This condition has been found in some substances like aldol in which a possible rotation of some group about a single bond could break the hydrogen bond. We have observed one alcohol in which this situation is possible, namely diacetone alcohol, and have compared it with tertiary amyl alcohol in which the immediate

environment of the O—H group is very similar, both substances being studied in CCl_4 solution. See Fig. 8. The former substance indeed shows a sharp band at λ9700 but it is very weak compared with the analogous one in the latter, certainly less than one-quarter as strong. We believe therefore that it would be quite unjustified to say that intramolecular bonds are absent in diacetone alcohol. Probably three quarters of the molecules are so bonded though in the remainder the linkage appears to be broken.

From general considerations as well as from known facts it appears to us reasonable to suppose that any hydroxyl group which is so little perturbed that it has about the same vibrational frequency as that found in the monomer alcohols will have also about the same ability to absorb. Consequently if a substance containing these groups has an unusually weak absorption in the regions where the O—H harmonic bands are usually found it is extremely probable that in a considerable fraction of the molecules the hydroxyl group has entered into a hydrogen bond.

General Character of the O—H Bands in Cases on the Intermolecular Hydrogen Bond

The work which has been described as well as the references which have been cited make it clear that in cases of the intermolecular bond involving hydroxyl hydrogen there is indeed a rather characteristic spectrum which can be ascribed to the vibrations of a modified O—H group. This differs somewhat in individual cases but in general one finds very broad bands with some structure which are considerably shifted to the low frequency side of the normal O—H harmonic bands. It seems worth while to discuss the probable reasons for the general character of these bands before considering the case of the intramolecular bond.

Now in those instances in which it is possible to observe the narrow O—H bands of the same substance in the two conditions it appears that in going from vapor to liquid or solution they are shifted to longer wave-lengths by an appreciable amount (about 100 cm^{-1} in the case of the third harmonic) but are not greatly broadened. The "association" bands on the other hand are distinguished by a breadth which is from ten to fifteen times greater. There may be several causes for this but the following list of five appears to us to include the more probable ones:

1. The association bands may not be due exclusively to a shifted O—H vibration but may arise in part from an alteration in frequency and intensity of other bands, or may indeed include combinations of C—H frequencies with intermolecular vibrations in the polymer.

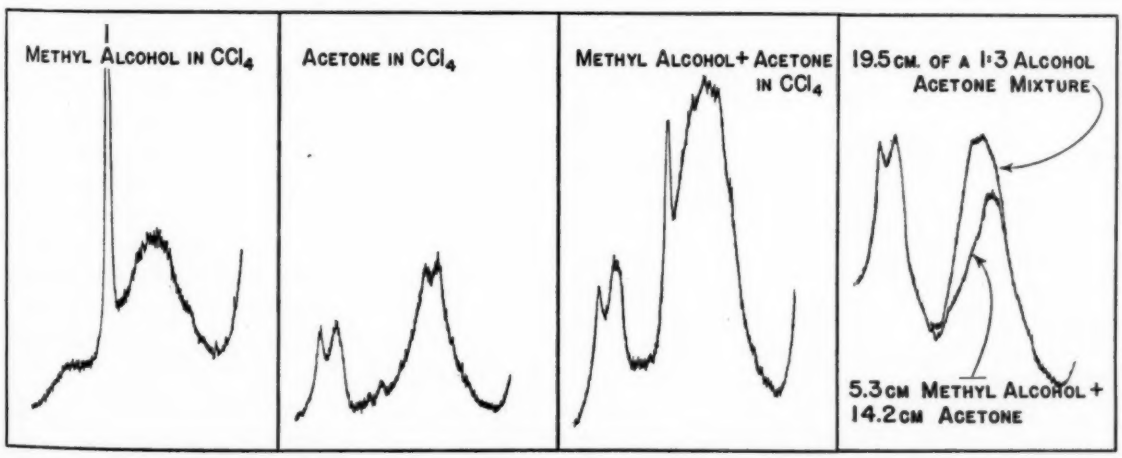
Methyl Alcohol in CCl_4
Acetone in CCl_4
Methyl Alcohol + Acetone in CCl_4
19.5 cm. of a 1:3 Alcohol Acetone Mixture
5.3 cm Methyl Alcohol + 14.2 cm Acetone

Fig. 7. Microphotometer curves demonstrating the formation of an intermolecular bond between methyl alcohol and acetone and the development of a new association spectrum. In the first three cases the path length was 75.8 cm and the concentrations were: (1) 5 cc methyl alcohol per 100 CCl_4, (2) 25 cc acetone per 100 cc CCl_4, (3) 5 cc alcohol and 25 cc acetone per 100 cc CCl_4. The lower curve of the last diagram was obtained with the two liquids in separate cells in series in the light path.

2. Several different polymers may exist simultaneously in which the situation of the O—H group is slightly different. It is evident from freezing point measurements as well as from vapor densities that in the case of the alcohols we have the situation known as the "continued equilibrium" in which a great number of different kinds of polymer are in equilibrium.

3. There may be combination bands of the O—H vibration with intermolecular vibrations. This would not be surprising since the interaction energy must be appreciable.

4. In the completely dissociated simple alcohols or acids we have a degenerate condition, with only one O—H frequency. When association takes place this degeneracy is partly removed and there exists in each polymer a number of modes of O—H vibration some of which may still be degenerate, but some of which will have different frequencies.

5. Since the hydrogen bridge is relatively very weak in comparison with other bonds there will exist in any polymer low frequency intermolecular vibrations in which the component molecules behave as practically rigid units and oscillate with respect to each other. Since these vibrations almost exclusively involve a stretching or bending of the hydrogen bonds they will interact greatly with the O—H vibration. Being of very low frequency they will on the average be nearly classically excited at ordinary temperatures, especially in the heavier molecules. As they are more and more excited, due to the character of the potential function the molecules will on the average be farther apart and the mean condition of the O—H groups will approach that in the completely dissociated state. Owing to the presence of polymers in various excited states we should expect at room temperature a greatly broadened band with upper limit near the O—H frequency of the monomer, and lower limit near the position which the band would have at very low temperatures. The absorption maximum, which must be in some way related to the most probable energy in the intermolecular degrees of freedom, would be expected to shift to higher frequencies as the temperature is raised.

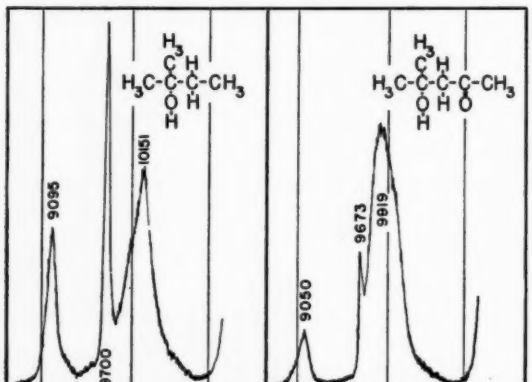

FIG. 8. Spectra of *tert*-amyl and diacetone alcohols in carbon tetrachloride solution. Concentration in each case was about 18.05 mole percent, and path length 75.8 cm.

It is not possible to give a general discussion of the first two reasons though in regard to the second we call attention to the studies of methyl alcohol at various concentrations. The association bands do not seem to change in character on increasing the concentration, but develop as a whole. It appears to us that even in rather dilute solutions the polymers present in any appreciable concentration are already sufficiently complex to possess practically all possibilities with regard to the O—H group which are found even in the liquid alcohol. Vapor density and freezing point data indicate that the tendency for association is small at the dimer stage but increases with higher polymers.

In any case we have studied some substances in which reasons 1 and 2 can scarcely play any part. In trichloracetic, sulfuric, and phosphoric acids the absence of C—H vibrations should make the spectrum in the λ10,000 region quite free of bands not involving the O—H vibration. In the solutions of the acids and possibly even in the liquid state the dimers should greatly predominate over any other polymer. But even in these cases the same broad character of the association bands is preserved indicating the importance of the remaining reasons. We shall now discuss points 4 and 5 in somewhat greater detail in the case of the organic acids which presents some particularly interesting possibilities.

DEGENERACY OF THE O—H VIBRATIONS IN THE ACID DIMERS

In the monobasic organic acids, which exist principally in the form of double molecules, we have an especially simple situation. In consider-

ing the O−H vibrations appropriate coordinates will be $(x_1+x_2)/2$ and $(x_1-x_2)/2$, where x_1 and x_2 are the displacements of the respective hydrogen atoms from their equilibrium positions, measured in the direction away from the oxygen atoms to which they are most strongly attached. In an approximate treatment we may regard them as normal coordinates since all of the molecule except the hydroxyl hydrogens will be comparatively rigid and motionless. Corresponding to the two coordinates there will be two frequencies which may be designated as ν_s and ν_a. If the double molecule possesses a center of symmetry, which is practically certain in the case of formic acid, ν_s will be infrared inactive while ν_a will be active. We shall expect only those infrared bands roughly given by the formula $\nu = V_s\nu_s + V_a\nu_a$ where V_a is odd, though V_s may take the value of any integer. Thus in the 3μ and 1.5μ regions we shall expect only ν_a and $\nu_s+\nu_a$ respectively, while near 1μ there will be two bands, $2\nu_s+\nu_a$ and $3\nu_a$. This is strictly true in formic acid while in heavier molecules which do not possess a center of symmetry it will be so nearly true that the bands mentioned will probably be the only ones strong enough to observe. It seems fairly clear that the association band of the organic acids near 1μ is a doublet though the temperature broadening makes it difficult to be certain. The 3μ and 1.5μ regions have not been investigated with sufficient dispersion to make the situation clear.

A consideration of the potential function of the molecule brings out some additional facts. See Fig. 9. If the hydroxyl hydrogens are indeed located on the lines joining the oxygen atoms which they link the potential energy will have two minima in $(x_1+x_2)/2$ and one only in $(x_1-x_2)/2$. From this it is clear that ν_a is probably of higher frequency than ν_s. For the development of the theory of the hydrogen bond it is important to have a more exact knowledge of the potential function, in particular of the height of the potential hump separating the two minima in $(x_1+x_2)/2$, but this will probably be rather difficult to obtain. The double minimum will of course give rise to a splitting of the energy levels, but on account of the diffuse character of the spectra it will probably be impossible to observe this except perhaps in the case of one or two

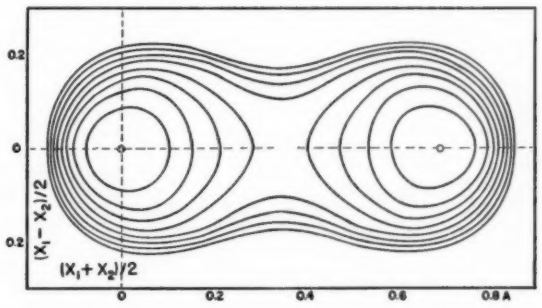

FIG. 9. Topographic diagram showing approximate dependence of the potential energy of the organic acid double molecule on two coordinates. The interval between contours is roughly 10,000 cal.

levels just below the potential hump. If one could make observations on high harmonic bands one might be able to come to some conclusion but there are experimental difficulties in the way.

BROADENING OF THE BANDS DUE TO THE INTERACTION BETWEEN THE O−H AND THE TEMPERATURE EXCITED INTERMOLECULAR VIBRATIONS

In the simplest case, the dimer of a simple monobasic organic acid, there are six vibrations, which we may call intermolecular, in which the hydrogen bonds due to their extreme relative weakness will be concerned almost exclusively. The two of highest frequency involve in the one case simultaneous stretching or compression of the two bonds (alternate approach and recession of the two component molecules), and in the other the stretching of one bond while the other is compressed. We may estimate force constants for the hydrogen bonds from the distance between the hydrogen atom and the oxygen to which it is weakly attached.[14] This separation must be roughly 1.71A, since the O−O distance is known to be 2.67A in the formic acid dimer[15] and the internuclear separation in the hydroxyl group cannot be much greater than in the water molecule. In the formic acid dimer the two high frequency internuclear vibrations will be of the order of 350 cm^{-1} and will have about 0.4 of classical excitation at room temperature.

In heavier molecules these frequencies will be considerably lower and excitation more nearly

[14] R. M. Badger, J. Chem. Phys. **2**, 128 (1934).
[15] Pauling and Brockway, Proc. Nat. Acad. Sci. **20**, 336 (1934).

complete while all other vibrations in all cases must be practically completely excited since they involve chiefly a bending of very weak bonds. This means that up to 3600 cal. per mole of dimer may be present in degrees of freedom involving hydrogen bonds even at ordinary temperatures. It is not surprising that the O—H association bands are extremely broad, and that O—H frequencies should so frequently be difficult to observe in the Raman spectrum.

We have attempted to observe temperature changes in the spectra of organic acids in carbon tetrachloride solution but the temperature range in which it was possible to work was somewhat restricted and our results were not conclusive. In the case of the liquid alcohols the shift of maximum with temperature was quite noticeable.

Expected Character of the O—H Bands in Cases of Intramolecular Hydrogen Bond

Unfortunately in the λλ9000–11,000 region we have found it impossible to make any very certain identification of bands due to an O—H group engaged in an intramolecular bond. As mentioned above, the aromatic compounds in which such bonds largely exist have combination bands near λ11,000, and in some aliphatic substances a similar difficulty was encountered since it was probable that combinations of C—H and C=O vibrations were responsible for a part of the absorption observed. However, in the regions of the fundamental and second harmonic the situation may be more favorable and it seems worth while to make some suggestions as to what may be expected in case observations can be made. The position of a band can probably be fairly accurately estimated if the bond energy is known, as will be shown below, but the character of the band may well be rather different from that of the association bands of the alcohols, etc.

As will be discussed below we see at the moment no spectroscopic evidence that the kind of interaction between the hydroxyl group and other atoms which produces a very considerable lowering of the O—H frequency in orthochlorophenol, or in the single molecules of acids in the vapor state, is to be distinguished from that found in the hydrogen bond in the commonly accepted sense, except that in the former case steric factors prevent the normal strength of the bond being realized. In the single molecules of formic or acetic acid the O—H bands though of about 300 cm^{-1} lower frequency than the methyl alcohol bands, in the case of the third harmonic, are sharp and of normal character. This is to be expected since there is only one vibration of the molecule which more or less exclusively involves the hydrogen bond and this will not be of very low frequency since it is a torsional motion of the light hydrogen atom about the ordinary O—H bond. In the great majority of the molecules this degree of freedom will not be excited and the factor responsible for the breadth of the association bands is absent.

The cases of intramolecular hydrogen bond in the ordinarily accepted sense will lie intermediate between the two extremes. In some instances there may be vibrations of moderately low frequency within the molecule which if excited will tend to break the bond, but the excitation will in general not be very great and the O—H bands will still be rather sharp. In nondegenerate cases we shall not expect any structure in the bands unless the O—H group is able to be found in more than one situation.

Conclusion

The various kinds of evidence which have been used to establish the presence of hydrogen bonds have sometimes led to contradictory conclusions but this should seldom be the case if one establishes really satisfactory criteria which have been compared with each other in a number of cases. In order to establish such criteria one must of course decide what is to be meant by a hydrogen bond. Shall the term be reserved for certain cases in which the O—O or other internuclear distance concerned and the energy required to break the bond lie within rather narrow limits, or shall it be extended to include a great variety of weaker interactions such as are responsible for the low frequency of vibration of the O—H group in single molecules of the acids and in orthochlorphenol, and for a part of the heats of vaporization of HCN and HCl? These latter, of course, merge into the group of interactions known as van der Waals forces.

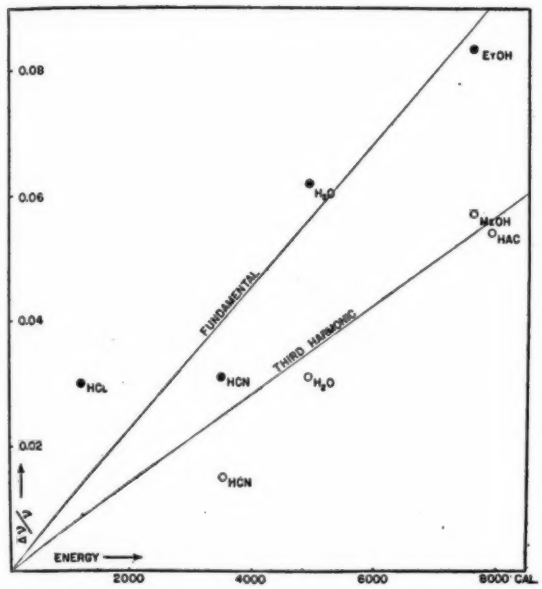

FIG. 10. Relation between frequency shift and interaction energy.

It would appear that the most satisfactory ultimate criterion for the presence of a bond is the energy required to break it, though of course one may decide to distinguish between different hydrogen bonds of the same energy and evidence may be forthcoming to show that this is desirable. So far as spectroscopic information goes we are at present only able to distinguish between cases by the magnitudes of the frequency shifts and by the intensity of absorption. Of the frequency shifts there appears to be a practically continuous series of cases from the small displacement when an alcohol vapor is dissolved in CCl_4 to ones so large that the O−H frequency approaches that of the C−H group.

We have mentioned some qualitative evidence that the shift of the O−H frequency is some measure of the strength of a hydrogen bond, or more generally of the magnitude of some interaction between hydroxyl hydrogen and another atom. It is unfortunate that the energies are known accurately in only a few cases, but we have collected some data which seem to be more or less reliable and present them in Fig. 10. In the organic acids and the alcohols the frequency shift plotted is the difference between the maximum of the respective association band and the frequency of the narrow band of methyl alcohol vapor, which was taken as standard or normal. In the other cases the shift is that observed in going from vapor to liquid. The energy data for acetic acid were obtained from the work of MacDougall.[16] In the other cases they were estimated from heats of vaporization. The procedure in the case of the alcohols has been outlined above. In water the energy of vaporization was assumed to be due practically entirely to the breaking of hydrogen bonds. In HCl and HCN one-half of the energies of vaporization of Cl_2 and $(CN)_2$ were subtracted from the energies of vaporization of the two liquids, respectively. The frequency shifts of the water band were taken from our own data in the case of the third harmonic, and from the Raman observations of Cross, Burnham and Leighton[17] for the fundamental.

It is seen that the frequency shifts are indeed a semiquantitative measure of the energies. Considering the nature of the bands in the associated acid molecules, for example, it is evident that there will be no very simple general relationship, but even if an approximate proportionality exists, as seems to be the case, it should be very useful. It is interesting that if the percentage frequency shifts of the water band observed by Cross, Burnham and Leighton are plotted against energy of vaporization, instead of against the temperature, the slope of the curve at lower temperatures is nearly the same as in our plot.

The plot in Fig. 10 suggests that corresponding to the series of frequency shifts there is a similar set of energy conditions, which would make it very arbitrary indeed to put definite limitations on the situation which is to be described as a hydrogen bond. If a few more energy data can be obtained to confirm the approximate relationship between shift and energy we believe that it will be very useful in the further discussion of many cases which have already been investigated, particularly those in which a number of subsidiary maxima accompany a weak absorption near 7100 cm^{-1}.

[16] F. H. MacDougall, J. Am. Chem. Soc. **58**, 2585 (1936).
[17] Cross, Burnham and Leighton, J. Am. Chem. Soc. **59**, 1134 (1937).

The O-H Band in the Vapors of Some Organic Acids and of Tertiary Amyl Alcohol in the Region λ9700*

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Absorption bands corresponding to the third harmonic of the O—H vibration have been observed in the vapors of formic, acetic, propionic and trichloracetic acids, with centers at about 10202.8, 10242, 10235 and 10250 cm^{-1}, respectively. Formic acid alone gave a band with resolvable fine structrue, but this has unusual features and may be described as a hybrid. The simultaneous presence of characteristics similar to those of both "perpendicular" and "parallel" type bands of symmetrical molecules is due to the fact that the change in electric moment produced by the O—H vibration has components along two of the principal axes of the molecule. Rotational constants for the formic acid molecule have been evaluated and the moments of inertia were found to be 85.2, 74.4 and 10.81×10^{-40} g cm^2. The structures of the organic acid molecules are discussed and a comparison is made with nitric acid. In *tert*-amyl alcohol a band with single broad maximum at about 10414 cm^{-1} was found.

EXPERIMENTAL

THE absorption cell used in the experiments here described consisted of a Pyrex cell 304.8 cm long, which was confined in a resistance furnace of somewhat greater length. The pressure of vapor in the cell was controlled by regulating the temperature of a side arm which contained an excess of liquid acid (or alcohol) and was provided with an auxiliary heater. The pressures and temperatures used were such that the vapors of the acids were largely dissociated and the spectra obtained are those characteristic of the single molecules as we have previously shown in the case of acetic acid.[1]

The spectrograms were taken in the first order of a 21 ft. grating using Eastman 144 Q plates which had been sensitized with ammonia. The iron lines in the second and third orders were used as calibration standards and a few weak water lines, due to traces of water vapor in the spectrograph, were also useful. In the case of formic acid two entirely independent sets of measurements were made which were found to agree very well. In one set the measurements were made directly on two plates with a comparator. In the other case microphotometer curves with a fivefold linear enlargement were used.

FORMIC ACID

The formic acid band at 10202.83 cm^{-1} has previously been observed by Herzberg and Verleger.[2] These workers have described the more prominent features of the band but apparently their resolving power was not quite adequate to bring out certain unusual and interesting details. Except for a small region near the center the structure at first sight appears to resemble that of the "perpendicular" type bands of a symmetrical rotator, and consists of a series of very well-defined pQ and rQ branches[3] between which a number of weaker and sometimes incompletely resolved lines are visible. See Fig. 1. Closer inspection shows that the features of a "parallel" type band are also present, though considerably less intense. This is immediately evident only in the series of qQ branches which starts from the band origin, though the presence of the "parallel" band appears to be responsible for a very considerable asymmetry in intensity distribution. The "hybrid" character of the formic acid band is evidently due to the fact that the change in electric moment produced by the O—H vibration is not parallel to any of the principal axes of the molecule but has components in the direction of two of them. Such composite bands are generally to be expected in molecules without true elements

* This investigation is a part of a program of research made possible by a grant-in-aid from the National Research Council to one of us (R. M. B.) for which it is desired to express appreciation.

[1] Badger and Bauer, J. Chem. Phys. **5**, 605 (1937).

[2] Herzberg and Verleger, Physik. Zeits. **12**, 444 (1936).

[3] In describing the formic acid band and in designating the rotational constants we shall use the nomenclature of Dieke and Kistiakowsky, Phys. Rev. **45**, 4 (1934).

of symmetry even though they may be nearly symmetrical rotators, but we know of no other case so far investigated in which the situation is as clear as in the one under discussion.

From the simplicity of the spectrum it is evident that the formic acid molecule is only slightly asymmetric and indeed the greater part of the band may be represented very accurately by equations of the same form as those applicable to the symmetric rotator. In the region where $K>3$ we find that the energy levels are fitted within experimental error by the equation: $W/hc=J(J+1)\delta+K^2(\gamma-\delta)+K^4\mu$. The rotational constants $(\gamma'-\delta')$, $(\gamma''-\delta'')$ and μ (which is the same for both upper and lower vibrational states) can be evaluated with satisfactory accuracy from the combinations between the maxima of the pQ and rQ branches which are presented in Table I. It seems permissible to make combinations between the maxima of the branches since they are very narrow and the lines composing them are almost perfectly superposed. The agreement between the observed qQ branches and those calculated from the rotational constants obtained from the other branches is remarkably satisfactory.

The accuracy of the constant δ is probably somewhat less since for its evaluation we were obliged to use the weak lines on either side of the band which we have mentioned above. These lines, in the regions in which they can be resolved, appear to form series with a constant spacing which is a submultiple of that of the pQ and rQ branches between which they lie. On one side of the band the series can be followed for 42 lines, and on the other for 38 lines. The average spacings are 0.700 and 0.693 cm^{-1}, respectively.

TABLE I. *Principal maxima in the formic acid band at 10202.83 cm^{-1}.*

K	$pQ(K)$	$rQ(K)$	$qQ(K)$	$\frac{rQ(K)-pQ(K)}{4K}$	$\frac{rQ(K-1)-pQ(K+1)}{4K}$
3	—	10217.53	—	—	—
4	10187.06	21.59	10202.00	215.81	220.00
5	82.33	25.55	01.76	216.10	219.90
6	77.60	29.47	01.27	216.12	220.29
7	72.68	33.35	00.76	216.67	220.10
8	67.84	37.08	00.15	216.37	220.21
9	62.88	40.70	10199.45	216.16	220.11
10	57.84	44.15	98.65	215.77	220.08
11	52.67	47.50	98.78	215.84	219.81
12	47.43	50.76	96.88	215.27	219.56
13	42.11	54.10	95.84	215.36	219.17
14	36.79	57.18	94.74	214.98	219.07
15	31.42	60.25	93.57	214.71	218.51
16	26.07	63.18	92.18	214.23	218.42
17	20.46	65.89	91.26	213.86	218.00
18	14.94		89.55		217.51
19	09.28		88.03		
20	03.66				

Band origin is at 10202.83 cm^{-1}.
$(\gamma'-\delta)=2.1697$ cm^{-1}; $\mu=-5.25\times10^{-5}$ cm^{-1}.
$(\gamma''-\delta)=2.2106$ cm^{-1}; $\delta=0.348$ cm^{-1}.
$A_0=85.2\times10^{-40}$; $B_0=74.4\times10^{-40}$; $C_0=10.81\times10^{-40}$ g cm^2.

These lines appear to result from the near superposition of several pP and pR or rP and rR branches. That they are moderately sharp and well resolved must be due to two more or less fortuitous circumstances. In the first place it is clear that the constant δ is practically the same in both initial and final vibrational levels. From the sharpness of the pQ, qQ and rQ branches we estimate that its change cannot exceed about 0.5 percent. This being the case the line spacing must be nearly constant throughout all P and R branches. In the second place this spacing happens to be a submultiple of the distance between pQ and rQ branches in the regions of the band where the weak lines are sufficiently intense to observe. We have taken the constant δ as half the average of the mean spacings mentioned above and believe that it is in error by not more than one percent.

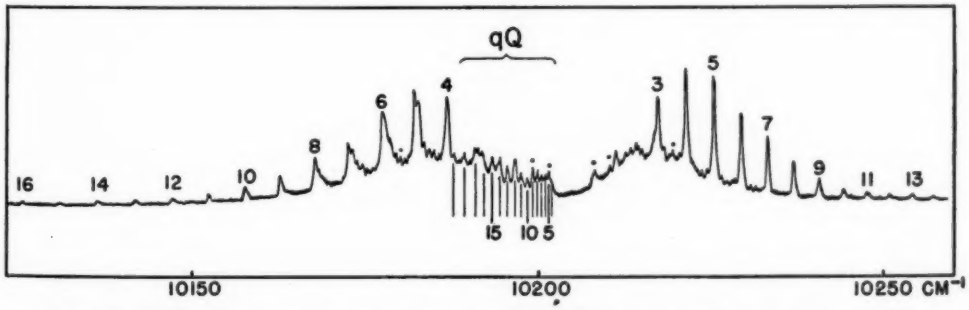

FIG. 1. Microphotometer curve of the O–H absorption band at 10202.83 cm^{-1} characteristic of the single molecules of formic acid in the vapor state. A few lines which may have slightly anomalous intensity due to a coincidence with weak water lines are indicated by dots.

In order to evaluate the moments of inertia of the formic acid molecule from the rotational constants it is necessary to have some knowledge regarding its shape. There seems to be no reason to doubt that the hydrogen attached to the carbon atom lies in the plane of the three heavy atoms, and the nature of the band observed makes it evident that the other hydrogen also lies in this plane. The appearance of the different bands which are possible in the case of a slightly asymmetric rotator has never been adequately discussed in the literature, but a consideration of an energy level diagram such as is given by Dieke and Kistiakowsky,[3] and of the selection rules, leads to the conclusion that in the formic acid band we are concerned with a case in which the change in electric moment has components in the direction of both *intermediate* and *minor* axes of inertia. The component in the direction of the minor axis must be comparatively small because of the relative weakness of the "parallel" type features of the band. That the principal component is in the direction of the intermediate rather than the major axis is evident from the considerable lack of intensity near the center of the band, as compared with the "perpendicular" bands of a symmetrical rotator, and from the absence of the rudimentary Q branch such as is present in the 10.5μ band of ethylene.

Since the direction of change of electric moment produced by the O−H vibration must be nearly parallel to the O−H bond the facts mentioned above are sufficient to locate the hydroxyl hydrogen in the plane of the other atoms and on the side of the molecule nearest to the oxygen atom to which it is not attached. If it were on the other side of the molecule the "parallel" type features of the band would predominate. Other convincing arguments lead to the same conclusion. The low frequency of the O−H vibration in formic acid as compared with methyl alcohol indicates a large interaction between the hydroxyl hydrogen and the oxygen to which it is not bonded. This interaction may very possibly be of the nature of that found in the hydrogen bond. No strong bond can be formed in this case because of the great distance between the atoms, but the plane configuration of the molecule must nevertheless correspond to a rather deep energy minimum since the torsional vibration of the hydroxyl hydrogen is evidently not excited to an appreciable extent. If this vibration were excited we should expect a number of overlapping bands arising from absorption by excited molecules, but there is absolutely no evidence of this.

Since the formic acid molecule is plane the moments of inertia A, B and C may be calculated from the relations $A=B+C$; $8\pi^2c\delta/h=(1/2)(1/A+1/B)$; $8\pi^2c\gamma/h=1/C$. Values are given in Table I. Unfortunately it is not possible to draw any very definite conclusions from these moments of inertia regarding the internuclear distances and bond angles of the molecule since there are seven parameters to be determined. It seems reasonable to assume that the C−H and O−H distances are approximately 1.07 and 0.96A, respectively, that the C−H bond makes nearly equal angles with the two C−O bonds, and that the angle between C−O and O−H bonds is in the neighborhood of 105°. Bonner and Hofstadter[4] have recently made a vibrational analysis of the formic acid spectrum and have evaluated approximate force constants for the two C−O bonds from which we may conclude that the respective internuclear distances cannot be greatly different from 1.43 and 1.24A. With any distances in the neighborhood of these the angle between the two C−O bonds must be close to 123° to obtain agreement with our moments of inertia. We find good agreement when the distance from the carbon atom to the hydroxyl oxygen is taken as 1.40A and the other C−O distance as about 1.25A.

It should be possible to make a definite statement regarding the orientation of the O−H bond if the ratio of intensity of the "parallel" and "perpendicular" features of the 10202.8 cm^{-1} could be estimated at all accurately. Unfortunately we have not been able to devise any satisfactory way to do this and though our estimate that the intensity ratio is around 1 : 16 suggests that the angle between C−O and O−H bonds may be a trifle less than 105° the probable error is far too great to warrant any definite conclusion being drawn.

Acetic, Propionic and Trichloracetic Acids

The O−H bands of these substances are represented in the microphotometer curves of

[4] Bonner and Hofstadter, Phys. Rev. 51, 1017 (1937).

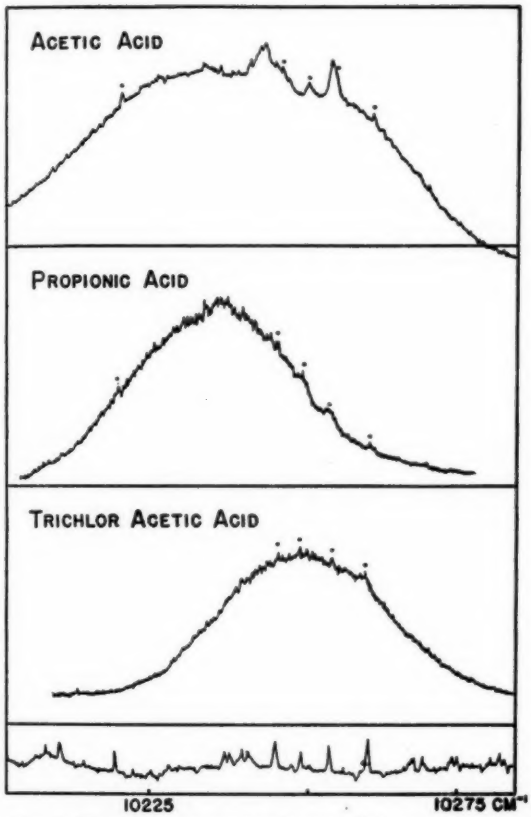

FIG. 2. The O–H absorption bands of three organic acid molecules in the vapor state. Some weak water lines are indicated by dots and the water spectrum is given for comparison at the foot of the figure.

Fig. 2. No fine structure was resolvable in any case and the bands of propionic acid and trichloracetic acid have smooth envelopes with a single maximum. In acetic acid there is a weak and somewhat broad Q branch near the center of the band and another similar peak on the high frequency side. The cause of this secondary peak is doubtful. From the fact that the O−H frequency is nearly the same in the four organic acids which we have studied we conclude that the configuration of the carboxyl group is similar in all of them.

Remarks on Nitric Acid

It is interesting to compare nitric acid with the organic acids. The O−H band of this substance at 10170.2 cm^{-1}, which we have previously described,[5] has a quite different appearance from those of the other substances and is quite unique in our experience in the narrowness and intensity of its Q branch. The presence of this feature makes it necessary to conclude that the nitric acid molecule is nearly a symmetrical rotator and furthermore that the change in electric moment produced by the O−H vibration is nearly perpendicular to both of the principal axes corresponding to the nearly equal moments of inertia. No reasonable model in which all the atoms lie in a plane will meet these requirements. The condition that the molecule be nearly a symmetrical rotator can be met by reasonable arrangements of the four heavy atoms in a plane but the requirement regarding the direction of the electric moment makes it necessary to assume that the O−H bond is inclined nearly normal to this plane. This seems a somewhat surprising situation but we see no way at the moment of escaping from the conclusion.

Tertiary Amyl Alcohol

The O−H band of this substance was found to have a smooth symmetrical envelope with a single broad maximum at about λ9600 (10414 cm^{-1}). From our previous study of the vapors of the alcohols[5] we had concluded that the O−H frequency depends very little on the mass of the molecule but is determined almost entirely by the type of alcohol (primary, secondary or tertiary). Our new observation lends support to this conclusion.

[5] Badger and Bauer, J. Chem. Phys. **4**, 711 (1936).

Concentration of N^{15} by Chemical Methods

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A study has been made on the application of chemical exchange reactions to the problem of the concentration of the nitrogen isotope of atomic weight 15. We have investigated the exchange reactions involving ammonia as the gas phase and solutions of ammonia in water and alcohol, and of ammonium nitrate and ammonium sulfate in water as the liquid phase. The apparatus used consists of an efficient type of fractionation column previously described. It is found that the exchange reaction between ammonium nitrate solution and ammonia is probably the best of all of these for this purpose, except that ammonium nitrate solutions corrode our steel column so badly that their use is impractical in the present apparatus. The exchange between ammonium sulfate solutions and ammonia gas is shown to be more satisfactory for the purpose than any of the other combinations, and has been used to secure a 6½-fold increased concentration of N^{15}. Substantial amounts of nitrogen containing high concentrations of N^{15} have been produced and these together with the efficient mass-spectrometer method of analysis make possible a wide variety of studies.

THE problem of the separation of the isotopes of the elements other than hydrogen has been studied for many years.[1] The methods which were first used depended upon differences in physical properties related directly to the masses. The method of diffusion was early used by Aston and by Harkins[1] and depends upon the differences in the rates of diffusion of light and heavy molecules. These authors used diffusion to produce a slight change in the relative abundance of the isotopes and repeated the process many times to secure a measurable effect. Hertz and his co-workers,[2] using the diffusion method, arranged successive diffusion units in a cascade system so that the lighter isotope was displaced toward one end and the heavy toward the other. In this way they multiplied the effect of a simple diffusion process many-fold and have produced very large changes in the relative abundance of neon, hydrogen and oxygen. Others[3] have used essentially the same method to produce changes in the relative abundance of the carbon and nitrogen isotopes. The mass-spectrograph method has been used by Rumbaugh[4] to secure practically complete separation of the lithium isotopes in very small amounts. Beams[5] using a centrifugal method has reported interesting and promising preliminary results. Huffman and Urey[6] have increased the concentration of H_2O^{18} by a factor of 4.5 by distillation of water. This method depends upon differences in vapor pressures of H_2O^{16} and H_2O^{18} discovered by Lewis and Cornish[7] and measured by Wahl and Urey.[8]

The marked differences in the chemical properties of hydrogen and deuterium, as well as the demonstration of differences in the vapor pressures of their compounds suggest the application of similar methods to the separation of other isotopes. Urey and Greiff[9] showed from theoretical calculations, that slight differences in the chemical properties of isotopic compounds of the lighter elements should exist, and Weber and Urey[10] have demonstrated that these theoretical calculations are confirmed in the case of the equilibrium between water and carbon dioxide with respect to the oxygen isotopic exchange. The separations that can be expected in the simple process equilibria of this type are very

[1] See Aston, *Mass Spectra and Isotopes* (Longmans, Green, New York, 1933), Chap. XVII.
[2] G. Hertz, Zeits. f. Physik **79**, 108, 700 (1932); **91**, 810 (1934); H. Harmsen, G. Hertz, and W. Schütze, Zeits. f. Physik **90**, 703 (1934).
[3] D. E. Woodbridge and F. A. Jenkins, Phys. Rev. **49**, 404, 704, 882 (1936); R. Sherr and W. Bleakney, Phys. Rev. **49**, 882 (1936); D. E. Woodbridge and W. R. Smythe, Phys. Rev. **50**, 233 (1936).
[4] L. H. Rumbaugh, Phys. Rev. **49**, 882 (1936).
[5] J. W. Beams and F. B. Haynes, Phys. Rev. **49**, 644 (1936); **50**, 491 (1936).
[6] G. B. Pegram, H. C. Urey, J. Huffman, Phys. Rev. **79**, 883 (1936); J. Chem. Phys. **4**, 623 (1936); J. R. Huffman and H. C. Urey, J. Ind. Eng. Chem. **29**, 531 (1937).
[7] G. N. Lewis and R. E. Cornish, J. Am. Chem. Soc. **55**, 2616 (1933).
[8] M. K. Wahl and H. C. Urey, J. Chem. Phys. **3**, 411 (1935).
[9] H. C. Urey and L. Greiff, J. Am. Chem. Soc. **57**, 321 (1935).
[10] L. A. Weber and H. C. Urey, J. Chem. Phys. **3**, 129 (1935).

slight, and indeed are smaller than those secured in diffusion, so that it is necessary to devise means for multiplying the effect of a single separation. Methods were outlined by Urey and Greiff for accomplishing this and preliminary experiments by Urey, Aten and Keston[11] and by Urey and Aten[12] have demonstrated their feasibility. In this paper we wish to report more extensive experiments designed to concentrate the heavy nitrogen isotope, using exchange reactions in which ammonia constitutes the gaseous phase and solutions of ammonia in water or methyl alcohol or of ammonium salts in water, constitute the liquid phases.[13] The exchange reactions which have been studied in this research are:

$$N^{15}H_3(g)+N^{14}H_3 \text{ (aq. sol.)} = N^{14}H_3(g)+N^{15}H_3 \text{ (aq. sol.)},$$

$$N^{15}H_3(g)+N^{14}H_3 \text{ (alcohol sol.)} = N^{14}H_3(g)+N^{15}H_3 \text{ (alcohol sol.)},$$

$$N^{15}H_3(g)+N^{14}H_4^+ \text{ (nitrate)} = N^{14}H_3(g)+N^{15}H_4^+ \text{ (nitrate)},$$

$$N^{15}H_3(g)+N^{14}H_4^+ \text{ (sulfate)} = N^{14}H_3(g)+N^{15}H_4^+ \text{ (sulfate)}.$$

For convenience we shall refer to these reactions by the symbols, NH_3-NH_4OH, NH^3-CH_3OH, NH_3, $NH_3-NH_4NO_3$ and $NH_3-(NH_4)_2SO_4$, respectively. Lewis and Macdonald[14] using two liquid phases instead of the gas and liquid phases as described here, have used essentially this same method in concentrating the light isotope of lithium.

In considering a successful method of concentrating the rare isotopes we must keep two factors in mind. In the first place, an appreciable concentration is desired; but what is meant by an appreciable concentration depends upon the uses for which the isotopic mixtures are being prepared. If the principal purpose is to study the properties of pure isotopic compounds, a nearly complete separation is desired. On the other hand, if they are to be used as tracers or for studying many exchange reaction problems, the extent of the separation is determined by the dilution factor in the experiments and the sensitiveness of the method of analysis. The method which we are describing in this paper has not as yet produced a concentration sufficient for convenient investigation of the physical properties of isotopic nitrogen but has produced concentrations which can be used for studies of many exchange reactions and biological problems.

The second requirement of a successful method for separating isotopes is that a sufficient amount of material be produced in a length of time which is not prohibitively long. The method of Hertz is able to produce highly concentrated materials, but only in amounts of the order of magnitude of a few cc of gas (S.T.P.) per 24 hours of operation. It is immediately obvious that no very extensive chemical or biochemical investigations can be made if only such small amounts of material are available. Thus the transport of heavy material per unit of time in the separating apparatus is of great importance. The method described in this paper has transported approximately 0.2 of a gram of N^{15} (100 percent) per 24 hours from natural nitrogen to nitrogen of a higher concentration. Even this is somewhat slow, when the production of sufficient amounts of material for the investigation of the physical properties of compounds of nearly pure N^{15} is undertaken.

The theory of the method used is essentially that of distillation in which a counter-flow of liquid and gas is maintained, condensation being used to convert the gas phase to the liquid phase and boiling to convert the liquid phase to the gas phase. Distillation columns have been used extensively for such distillation processes, and can be applied to the method of chemical exchange reactions in which we have a gaseous substance which can come to equilibrium with a liquid phase. The gaseous phase in the case of our problem consists of ammonia gas mixed with some water vapor or methyl alcohol vapor, and the liquid phase consists of a solution of ammonia in water or in alcohol, or of an ammonium salt in water. The process consists in a flow of the liquid phase downward through a fractionating column of high efficiency, liberation of the ammonia at the bottom of the column by boiling, or by the addition of sodium hydroxide and subsequent boiling, and the return of the ammonia upward

[11] H. C. Urey, A. H. W. Aten, Jr., and A. S. Keston, J. Chem. Phys. **4**, 622 (1936).
[12] H. C. Urey and A. H. W. Aten, Jr., Phys. Rev. **50**, 575 (1936).
[13] H. C. Urey, M. Fox, J. R. Huffman, H. G. Thode, J. A. C. S. **59**, 1407 (1937).
[14] G. N. Lewis and R. T. Macdonald, J. Am. Chem. Soc. **58**, 2519 (1936).

through the column. The maximum difference in concentration which can be secured in a distillation with total reflux is given by the formula

$$\frac{N_0}{1-N_0}\Big/\frac{N}{1-N}=\alpha^k, \tag{1}$$

in which N and N_0 are the mole fractions of one constituent, at the two ends of the column, α is the simple process fractionation factor (ratio of vapor pressures of the pure constituents) and k is the number of theoretical plates. This equation is really a definition of k, but general experience with distillation columns shows that k is proportional to the length of the column and that the distribution in the column at equilibrium is given by (1) if k is set equal to a constant multiplied by a distance from one end of the column. As we shall show, the value of α for the exchange reaction $NH_3-NH_4^+$ is about 1.02, and hence in order to produce a large ratio of the concentrations at the top and bottom, the value of k must be large.

The transport of a constituent in a column is equal to the quantity flowing in one direction multiplied by the mole fraction of the constituent in this phase minus the quantity flowing in the opposite direction multiplied by the mole fraction in that phase. When a steady state is reached the transport is the same at all points along the column. If there is no forward flow, i.e., no concentrated material removed, the transport, when in the steady state, is of course zero. Before the steady state is reached, the transport is not constant throughout the column, since a redistribution of material in the column is taking place. In the experiments which we are reporting, the column operates under these last conditions at the beginning; and at the end the steady state without forward flow exists and zero transport results. During the first part of the run a part of the column has very little or no variation in concentration along its length and hence there is adequate time for the two phases to come to equilibrium. Since the top part of the column is fed with natural isotopic ammonium salt or ammonia in water or alcohol solution, the transport can be calculated for this part of the column and is

$$T=w(N-n),$$

where w is the flow per unit time and N and n are the concentrations of N^{15} in the liquid and gas phases, respectively. Since equilibrium is established in this region,

$$\frac{N}{(1-N)}\Big/\frac{n}{(1-n)}=\alpha \tag{2}$$

and hence, when N and n are both small compared to unity and nearly equal as in the present case,

$$T=wN(\alpha-1). \tag{3}$$

The question as to the effect of fluctuations in the rate of flow on the transport must be considered since we cannot keep the rate of flow constant to within better than about five percent. The transport when the upward and downward rates of flow are not the same is

$$T=WN-wn,$$

so that fluctuations in W, the downward rate of flow, and w, the upward rate of flow will cause fluctuations in the transport and may easily change its sign. However, since the mean values of W and w must be the same when operating without forward flow, the mean transport must be that given by Eq. (3).

Huffman and Urey[6] have shown that the approach to the steady state in a column operating without forward flow and with an infinite reservoir at one end is given by the formulae

$$(1-N)\ln\frac{1-N}{1-N_0}+N\ln\frac{N}{N_0}=Kt, \tag{4}$$

$$K=\frac{wN(\alpha-1)k\ln\alpha}{H}, \tag{5}$$

where N is the mole fraction of N^{15} in natural nitrogen at one end of the column, N_0 the mole fraction of N^{15} at the other end, H is the hold-up i.e., the amount of material held in the column during operation, t is the time, and the other symbols have the meaning previously assigned. This formula is derived on the assumptions, (1) that the column may be divided into two regions, one toward the higher concentration end in which the distribution of the constituents is that for a column of that length in a steady state without forward flow and the remainder at the lower

concentration end, in which at any time the concentration is a constant (practically that of natural nitrogen) along this length, and (2) that the hold-up beyond the column at the high concentration end is negligible. If this hold-up, h, is not negligible, Eq. (4) becomes

$$(1-N)\ln\frac{1-N}{1-N_0}+N\ln\frac{N}{N_0}+k\frac{h}{H}(N_0-N)\ln\alpha = Kt. \quad (6)$$

Our experiments follow these formulae fairly closely and indicate that the assumptions used in their derivation are approximately correct.

Experimental

The distillation columns used in this work were suggested by Pegram[6] and were described by Huffman and Urey;[6] the reader is referred to this publication for a detailed description. The columns contain a succession of alternate stationary and rotating metal cones. We used a large steel column 35 feet high and 6 inches in diameter containing 621 pairs of cones and for control experiments a copper column $1\frac{1}{2}$ feet high, 6 inches in diameter containing 15 such pairs of cones.

The solution is pumped into the top of the column by means of a reciprocating piston pump with adjustable stroke driven by a synchronous motor and adjusted to pump the desired number of cubic centimeters of liquid per minute. See flow sheet in Fig. 1. The liquid draining from the bottom of the column is pumped to a mixing chamber at the top of a stripping column. This stripping column is placed on the upper floor, necessitating a pumping height of 40 feet. In order to minimize the hold-up at the bottom of the main column, the pump must have an excess capacity so that no accumulation of liquid takes place, and hence must be self-priming. In addition, this pump must handle any solid material such as iron oxide that drains from the column. After trying several types of pumps, a turbine pump was found to operate satisfactorily providing an additional 200 cc of water were fed into the pump per minute. This addition of water also decreases the hold-up in the pump and pump line. The packing gland of the turbine pump is kept wet by feeding water to it from a 500 cc reservoir of water; the water lubricates the gland and prevents air leaks. A solution of sodium hydroxide is fed by means of another piston type pump into the mixing chamber in order to liberate ammonia. This solution then flows into a small stripping column, consisting of a 7-foot length of 4-inch pipe packed with clay cylinders, $\frac{5}{8}$ of an inch in diameter. At the bottom of this column 200 cc of water are boiled per minute by means of a steam pot boiling at 45 lb. steam pressure in order to remove the last traces of ammonia from the solution. At the top of the stripping column and parallel to the mixing chamber there is a coil condenser to reflux the water boiled. The efficiency of this small column for removing the last traces of ammonia before the waste solution leaves the apparatus is very important. A loss of 20 parts of ammonia per million at the speeds we are using would be sufficient to limit the maximum concentration to 2.5 percent no matter how efficient the column. Tests on the waste solution from this stripping column made from time to time showed a content of 1 part of ammonia per million. The tests were made simply by warming without boiling a definite amount of the alkaline waste solution in a beaker covered with watch glass having a piece of wet litmus paper on its lower surface and noting the time for a color change. This was compared with similar tests using standard ammonia solutions. With reasonable care the test is quite reproducible. The spent solution of sodium sulfate runs to waste through a vertical pipe sufficiently long to permit drainage from the apparatus against the external atmospheric pressure. The liberated ammonia gas is returned to the bottom of the main column, and escapes at the top to be absorbed in water and wasted. This absorption chamber consists of a 3-foot length of 3-inch pipe packed with iron staples and furnished with an inlet for water and a vacuum leg to the sewer.

The small fractionating column is operated in much the same way. An ammonium salt solution pumped in at the top drains down through the column into a five liter flask containing an amount of sodium hydroxide sufficient to liberate the ammonia from its salt over the period of the run. The flask is kept boiling by means of a gas

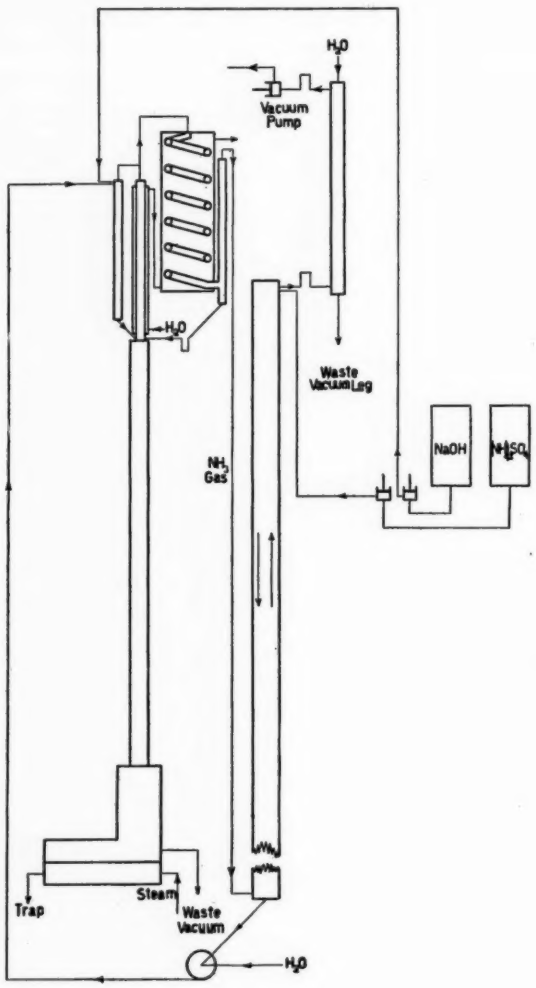

FIG. 1.

burner. A condenser is used above the flask to reflux the boiled water. In this way most of the ammonia is boiled out of the solution and the ammonia gas passes into the lower end of the column and escapes at the top. In all the small column runs equilibrium is established in from three to five hours. Since the column is not vacuum tight, nitrogen gas is led into the flask and passes through the system for the purpose of lowering the partial pressure of the ammonia gas. This decreases the hold-up of ammonia in the flask as well as the concentration of dissolved ammonia in the ammonium salt solution. The experiments are run under conditions of total reflux at the bottom until equilibrium is established.

ANALYSES

Analyses are made with the Bleakney[15] type mass spectrometer working with N_2 gas. Samples of NH_3 gas taken at the lower end of the column are dissolved in water and converted into nitrogen by the addition of a solution of sodium hypobromide. Air is removed by first freezing the separate solutions and pumping out the air with a mercury diffusion pump. Approximately 10 cc samples of nitrogen gas (S.T.P.) are used, though smaller samples would be satisfactory. The relative intensities of the mass 28 and mass 29 peaks are taken as the measure of the relative abundances of N_2^{14} and N^{15}. If this ratio is x then the mole fraction of N^{15} is easily seen to be $1/2x+1$.

The mass spectrometer is especially convenient for analysis since the mass 28 and mass 29 peaks are practically completely separated by our instrument. Since this is found to be true it is unnecessary to make corrections for overlapping of peaks. The determination of the relative abundance of the N^{14} and N^{15} isotopes in the same sample of nitrogen varies from day to day, ranging from 128.6 to 133.9 for the ratio of N_2^{14} to $N^{14}N^{15}$ for natural nitrogen. If we accept 0.38 as the percentage of N^{15} in nitrogen,[16] this ratio should be 131.0. The ratio is determined for ordinary nitrogen on each day that analyses are made, and the corresponding ratios for unknown samples are corrected for the deviation of natural nitrogen from the value of 131.0. Variations in the ratio $N_2^{14}/N^{14}N^{15}$ for natural nitrogen from day to day are due partly to experimental error and partly due to impurities which cause variations in the background intensity of mass peaks 28 and 29. The background intensity is small if the apparatus is well baked out before measurements are made and then the ratios run close to 131. An average value of 131.8 was obtained for this ratio in ordinary nitrogen over 34 different days. A potentiometric method is used to determine the peak intensitities in order to avoid difficulties due to the nonlinearity of the amplifying circuit. The ion collector plate is connected through an approximately 10 megohm resistance to a potentiometer which is then connected to

[15] W. Bleakney, Phys. Rev. **40**, 496 (1932).
[16] *International Table of Stable Isotopes for 1936* (Paris, 1936).

ground. With no back potential from the potentiometer, the potential of the collector plate will be proportional to the ion current though due to nonlinearity of the amplifier the deflection of the galvanometer will not be proportional to the intensity. However, the potentiometer can be used to bring the potential of the collector plate when ions are coming to it to the potential it has when no ions arrive at the plate. The measurement consists in setting the mass spectrometer off a peak, noting the position of the galvanometer in the amplied current circuit, then moving to a peak and by means of the potentiometer bringing the potential of the collector plate to the same value it had when off the peak, i.e., the galvanometer swing is brought to the position it had when off the peak. The resistances in the potentiometer are then a measure of the peak intensity above that of the background and no question of linearity of the amplifying circuit is involved. In our measurements we have used the mass spectrometer settings at masses 26.5 and 30.5 to secure the background readings for the 28 and 29 peaks, respectively. Typical readings for natural nitrogen and one of our concentrated samples are given in Table I. It will be seen that the readings are very reproducible, and that the ratio can be determined within a probable error of about 1 percent.

Results

A number of control experiments made with the small column from time to time are presented in Table II. In each run several samples were taken to make sure that equilibrium had been established but only the final concentrations are tabulated. If N_0 and N are small compared with unity, Eq. (1) can be written,

$$\log N_0/N = k \log \alpha.$$

The values of $k \log \alpha$ as given in the table are the experimental results, since both k and α cannot be determined from these experiments alone.

Table I.

Ordinary Nitrogen			Concentrated Sample	
Mass Peak	Intensity in Arbitrary Units	Ratio	Intensity in Arbitrary Units	Ratio
28	0.01146	130.8	0.0672	20.25
29	1.500		1.360	
28	0.01150	131.3	0.0695	20.08
29	1.510		1.395	
28	0.01157	131.4	0.0705	20.08
29	1.521		1.418	
		Av. 131.2		Av. 20.14

We use 1.006 as α for the exchange reaction NH_3-NH_4OH as found by Urey and Aten[12] and 1.021 for the exchange reaction $NH_3-(NH_4)_2SO_4$, (31 percent solution), as found in the subsequent work reported below. For comparison it is assumed that α for the exchange reaction $NH_3-(CH_3OH, NH_3)$ is 1.006. The values of k and α given in the last two columns are calculated by making various assumptions. The values of k for runs 1, 2, 3, and 4 are secured from $k \log \alpha$ by using the above values for α. Using 1.021 for α as given above the value 8 is calculated for k in run 7. This value of k is then assumed for runs 5, 6, and 8 and the values of α are calculated. Throughout the table the use of parentheses indicates assumed values.

Runs 1 and 2 give nearly the same result, indicating that for the NH_3-NH_4OH exchange the partial pressure of ammonia is unimportant. Run 3 shows that a methyl alcohol solution of ammonia is better than ammonium hydroxide for concentrating N^{15}. Comparing run 4 with run 3 it is seen that the over-all fractionation factor is decreased by doubling the liquid velocity, keeping the partial pressure of N_2 about the same. This means the efficiency of our column or the number of theoretical plates will depend upon the feed velocity. Runs 5, 6, 7, and 8 show that high salt concentrations are desirable. In each case the solutions are saturated with dissolved ammonia under the conditions of the experiment, and thus the concentration of ammonia is about the same, though the total concentration of nitrogen as ammonia and ammonium ion increases from Run 5 to Run 8. The values of α increase in Runs 5, 6, 7 and 8 because the large α for the $NH_3-(NH_4)_2SO_4$ exchange increases the experimental α above the low value of the α for the NH_3-NH_4OH exchange. It would be most desirable from the standpoint of operation and expense, to use NH_4OH in concentrating N^{15}, since no sodium hydroxide would be necessary and a considerable fraction of the NH_3 could be

TABLE II.

RUN	FEED SOL.	LIQUID VEL. IN cc/min.	N_2 VEL. IN liters/min.	N_0	$k \log \alpha$	α	k
1	NH_4OH	6.0	0	0.00396	0.0179	1.006	7.
2	NH_4OH	6.3	2	.00399	0.0212	1.006	8.1
3	CH_3OH-NH_3	5.0	1	.00408	0.0309	(1.006)	11.6
4	CH_3OH-NH_3	10.2	1.4	.003966	0.0186	(1.006)	7
5	5% $(NH_4)_2SO_4$	4.4	2	.00401	0.0234	1.0067	(8)
6	14% $(NH_4)_2SO_4$	4.2	2	.00412	0.0351	1.012	(8)
7	31% $(NH_4)_2SO_4$	4.4	2	.00449	0.0725	1.021	8
8	34% $(NH_4)_2SO_4$	4.3	2	.00453	0.0763	1.022	(8)

TABLE III.

Run	9	10[a]	11	12	13	14
Feed Solution	60% NH_4NO_3 in water	6.75% NH_3 in water	6.8% NH_3 in water	7% NH_3 in water	6.65% NH_3 in CH_3OH	15% $(NH_4)_2SO_4$ in water
Pressure cm of Hg	18	40	18.1	15	27	20
Feed Velocity cc/min.	108	75	98	10.4	12.2	10
Temperature	Room	60°C	Room	Room	Room	Room
Results	Hrs. Conc. N^{15}	Hrs. Conc. N^{15}	Hrs. Conc. N^{15}	Hrs. Conc. N^{15}	Hrs. Conc. N^{15}	Hrs. Conc. N^{15}
	0 0.38	0 0.38	0 0.38	0 0.38	0 0.38	0 0.38
	6 0.565	5 0.389	4 0.407	3.75 0.399	3 0.407	3 0.418
	10 0.632	10 0.405	7 0.424	7.25 0.418	6.25 0.422	6.5 0.446
		14 0.415	10 0.458[b]	10.25 0.429	9.5 0.437	10 0.468
		16 0.411	13 0.445		10.75 0.440	
			14.5 0.448			
K[d]	2.99×10^{-5}	0.456×10^{-6}	1.92×10^{-6}	1.58×10^{-6}	2.00×10^{-6}	4.25×10^{-6}
α	1.021	—	1.006	1.006	1.006[c]	1.012[c]
k	28.8	—	24.7	207	207	135

[a] The plot of the results of Run 10 does not give an approximate straight line, hence the value of K is very uncertain and values of α and k cannot be given.
[b] This analysis is probably in error since this point alone does not lie on the straight line. It is ignored in securing the value of K.
[c] Since the value of α is a pure assumption the value of k is also. This is included only to indicate the superiority of Run 13 over Run 12.
[d] In drawing straight lines through the plots, we find that the best straight line does not pass through the origin. This we believe is due to some irregularity at the beginning of the run. In calculating k, the value of H is taken as 4480 cc as determined in the case of Run 10.
[e] This was taken from Table II.

refluxed at the top of the column. These advantages, however, are more than compensated by the much higher fractionation factor found for concentrated salt solutions. The methyl alcohol solution of ammonia used in Runs 3 and 4 gives a better fractionation than the water solution of ammonia of Runs 1 and 2, but it does not appear to present a better method of concentration than the use of water solutions of the ammonium salts.

A number of preliminary runs were made with the large column. The results and conditions of the experiments are summarized in Table III. The values of k listed in the table are secured by plotting the function

$$(1-N)\log\frac{1-N}{1-N_0}+N\log\frac{N}{N_0}$$

against the time, drawing the best straight line through the points and taking the slope of this line as the value of K. The plots are shown in Fig. 2 and indicate how closely the relation of Eq. (6) is followed by our results. After Run 10, the column was drained, washed with water and the total hold-up of ammonia determined. This showed that the hold-up amounted to 4480 cc of the solution used. This value of H and the values of α given in the table are used to calculate k from the values of K secured from the plots. The value of α for the NH_3-NH_4OH exchange is that secured by Aten and Urey. The value of α ($=1.021$) used for the $NH_3-NH_4NO_3$ exchange is taken from subsequent experiments in which $(NH_4)_2SO_4$ is used, and may not be the correct value for this case. Finally, the value of k in Run 13 depends on the assumption of a value of α and may not be correct. The increase in concentration is small in all cases and due to

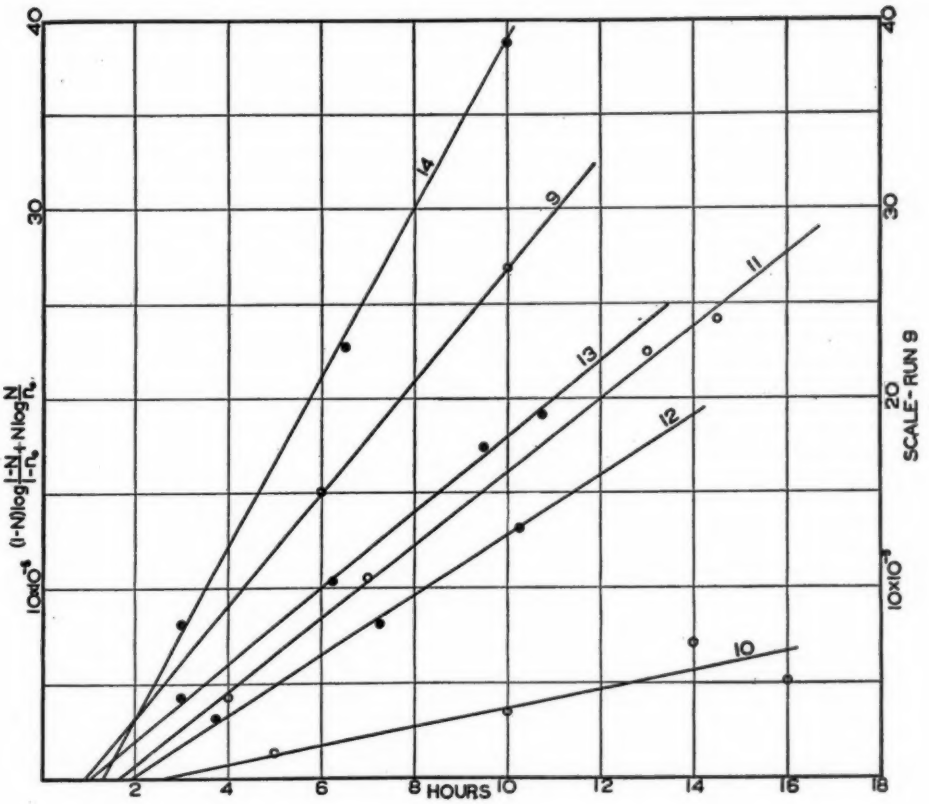

FIG. 2.

analytical errors, none of the derived constants can be regarded as very precise.

Ammonium nitrate was chosen in Run 9, because of its high solubility as well as the high solubility of sodium nitrate. The small value of k is very disappointing in view of the fact that the small column operates with 8 plates for $NH_3-(NH_4)_2SO_4$. However, the feed velocity used in Run 9 is more than 20 times that used in the small column runs. It was decided, therefore, to make a number of preliminary experiments to find out what liquid velocity should be used to give a reasonable number of plates with the large column. NH_4NO_3 had to be abandoned in these experiments because of severe corrosion. Although the fractionation factor for the exchange reaction NH_3-NH_4OH is much less, NH_4OH was more satisfactory in the test experiments. Runs 11 and 12 were run with feed velocities of 98, and 10 cc per minute, respectively. Decreasing the feed velocity, increased the number of plates, the number of plates being inversely proportional to the feed velocity within the limits of error. Run 10 was made with 60°C with the hope that a higher temperature would speed up the exchange reaction and therefore yield a larger number of plates. It is evident from a comparison of Runs 10 and 11 that the higher temperature is not of advantage. There are compensating factors at work here since the value of the fractionation factor, α, probably decreases with temperature whereas the speed of the reaction increases. The solution of ammonia in methyl alcohol used in Run 13 was found to be more effective than NH_4OH, but it appears that the rate and degree of concentration are not sufficiently high to justify the use of ammonia-alcohol solutions instead of the ammonium salt solutions as is easily seen from a comparison of Runs 9 and 13. This checks the results from the small column. These results though qualitative show that the $NH_4^+-NH_3$ exchange must be used and that the rate of flow using ammonium nitrate might be as high as 40 cc per minute if 2 percent or 3 percent N^{15} is desired. However, because of the

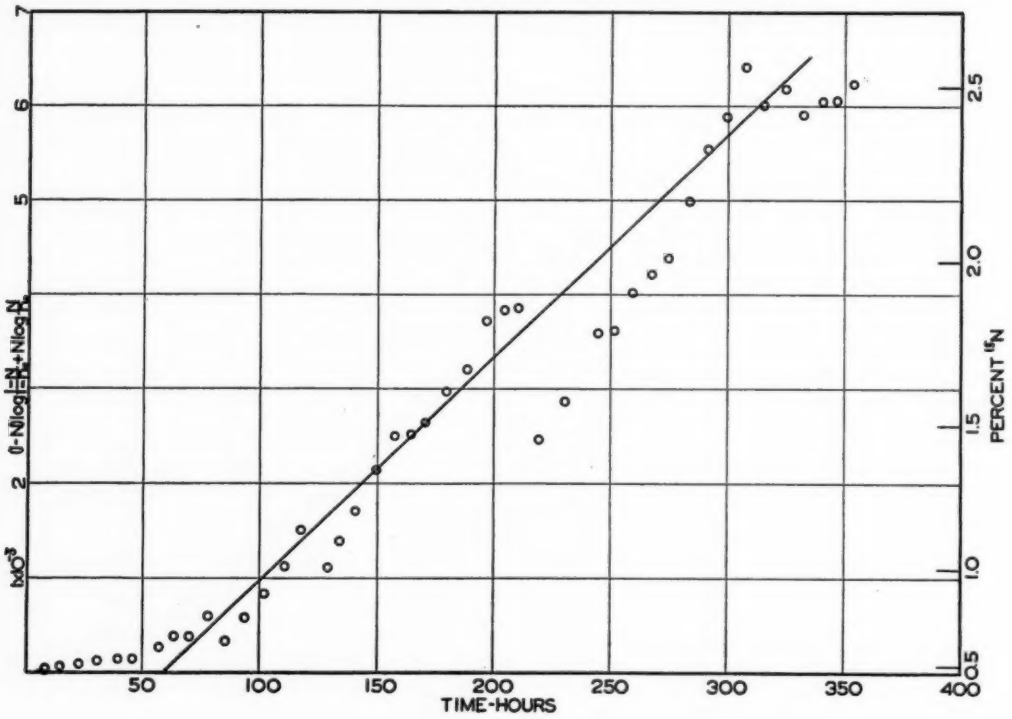
TIME-HOURS
PERCENT ^{15}N
$kx10^{-3}$
$(1-N)\log\frac{1-N}{1-N_0}+N\log N_0$

FIG. 3.

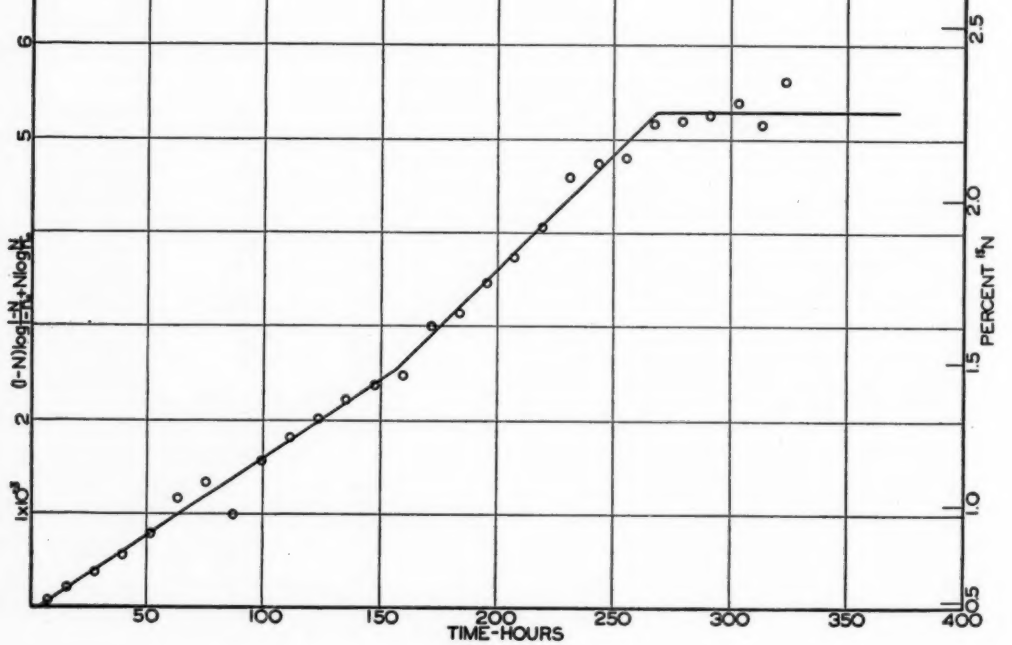
TIME-HOURS
PERCENT ^{15}N
$kx10^{-3}$
$(1-N)\log\frac{1-N}{1-N_0}+N\log N_0$

FIG. 4.

rapid corrosion we concluded that ammonium sulfate should be used in our column and that the rate of flow should be about 15 cc per minute as judged from Run 14.

Two final runs were made by feeding 15 cc/min. of a solution of ammonium sulfate (31 percent by weight) operating the entire apparatus at 8 cm of mercury pressure. Vacuum is used to cut down the concentration of dissolved ammonia and the amount of ammonia in the gas phase. Hence the working hold-up of the column is lowered so that less time is taken to effect a given separation. Low concentration of ammonia gas and low pressures are also important for the removal of ammonia from the solution in the stripping column. Ammonium chromate equivalent to 1 percent of the ammonium sulfate was added to the feed solution to decrease corrosion, and in Run 15 1 percent of methyl alcohol was added since this seemed to cause an oily film on the solution of the commercial ammonium sulfate to dissolve. During the first 150 hours of Run 16 we added no alcohol and for the remainder of the run, 5 percent of methyl alcohol.

In each of these runs the column was kept in operation until no further increase in the concentration of N^{15} was apparently obtained. A maximum concentration of 2.5 percent was reached in Run 15, and 2.34 percent in Run 16. The runs lasted about 12 days each. Ammonia gas samples were taken at the lower end of the column at intervals of from 8–12 hours, and the concentration of N^{15} determined on the mass spectrometer. The results are represented in Figs. 3 and 4. On the right-hand side of the figures the corresponding percentages of N^{15} are indicated.

The pressure in Run 15 was lowered from 20 to 15, to 10.8, and finally to 8 cm of Hg after 45, 85, and 280 hours of operation, respectively. Three interruptions occurred in this run; the steam pressure in the building was shut off, it was necessary to repair the small stripping column, and the feed pump gave trouble. A sharp break in the curve occurs at each interruption. However, the concentration increased until it reached 2.5 percent. The second run proceeded with but minor interruptions. The alkali pump was accidently shut off for twenty minutes. However, the ammonium sulfate lost in the waste from the stripping column was saved and fed back into the bottom of the column. The effect was to put one point off the curve at 87 hours. This curve follows the formula of Huffman and Urey rather well. The addition of 5 percent methyl alcohol after 150 hours increased the slope as can be seen from the curve indicating that the alcohol improved the operation somewhat though it did not increase the final concentration secured.

Knowing the total hold-up of the column and its average concentration, it is possible to calculate the amount of N^{15} transported during the run. On the completion of each of these runs the total hold-up of ammonia was determined by draining and washing the columns with water. A composite sample of all the drainings and wash waters was made up and analyzed. The hold-up in the pump, pump line, and condenser were also determined and analyses made. Table IV gives the results of these analyses and the amounts of NH_3^{15} transported. Using Eq. (3) it is possible to calculate α. The flow, w, in moles was calculated from the known rate of supply of ammonium sulfate including an estimate of the amount of ammonia dissolved in the solution. The duration of the run was taken as the time from the beginning of the run to the time at which the curves of Figs. 3 and 4 became approximately horizontal, namely, 320 and 268 hours for Runs 15 and 16, respectively. In this way we calculate α to be 1.013 and 1.021, respectively. It appears that considerable losses occurred in Run 15 due to the serious interruptions.

During Run 16 samples of the feed and of the ammonia gas escaping from the top of the column were taken at various times and the concentrations of N^{15} determined. Hence the value of α defined by Eq. (2) can be calculated since these concentrations should differ by one fractionation. The mean value of α secured from ten such analyses is 1.023. This is in satisfactory agree-

TABLE IV.

Run	Column Hold-up Moles NH_3	Analysis % N^{15}	Pump Hold-up Moles NH_3	Analysis % N^{15}	Moles $N^{15}H_3$ Transported
15	72.8	0.486	1.30	2.50	0.105
16	98	0.48	2.19	2.34	0.141

ment with the value calculated above though we believe that both values are uncertain because of the great difficulties involved in the determinations.[17]

The rate of attainment of equilibrium as given by the slope of the curve of Fig. 4, is greater than that to be expected from the final concentrations obtained. The slope

$$K=\frac{Nw(\alpha-1)k\log\alpha}{H}=2.36\times10^{-5}.$$

H thus calculated is 2479 cc, or about one-fifth the measured value of 13,050 cc for Run 16. This would be true if only one-fifth of the column at the lower end were working. We have no satisfactory explanation of this discrepancy since in all other tests of this relationship satisfactory agreement has been secured. It may be that the final steady state has not been attained in these runs in spite of the apparently horizontal character of the plots of Figs. 3 and 4 near the ends of the runs.

The hold-up was particularly large in both runs, amounting to approximately 10 liters in Run 15 and 13 liters in Run 16. In experiments on the distillation of water, and the bicarbonate-carbon dioxide exchange reaction, as well as for the exchange reaction NH_3-NH_4OH, the hold-up was approximately 4 to 4.5 liters. It may be that the large hold-up in the ammonium sulfate runs was due to corrosion which produced a considerable amount of iron oxide in the column, but this does not explain the discrepancy between the measured and calculated values of H mentioned above.

Using the values of $k\log\alpha$ obtained from the maximum concentrations secured in these two runs and the values of α as given above, the numbers of theoretical plates for Runs 15 and 16 are 91 and 85, respectively. These are about what one would expect from the values secured in the shorter runs with the large column as recorded in Table III.

On the completion of each run 1500 cc of solution were drained from the column in 100 and 200 cc batches, in order to avoid mixing the concentrated material with the more dilute from higher up in the column. Samples from the two runs were analyzed for N^{15} and batches of nearly the same concentration combined. The ammonium sulfate solutions were boiled with alkali and the liberated ammonia absorbed in hydrochloric acid. The resulting solutions were evaporated to dryness. The two runs yielded 61 grams of ammonium chloride containing 2.5 percent N^{15}, 244 grams in which the concentration of N^{15} was better than 2 percent, and 1087 grams in which the concentration of N^{15} ranged between 0.7 percent and 1.5 percent.

Conclusions

The apparatus which we have described and used in these experiments has certain marked advantages over those previously used. It is capable of a very much larger transport than that of the Hertz method, the transport being approximately 100 times as great, so that appreciable amounts of material can be produced and in the two more successful runs described, substantial amounts of N^{15} of sufficiently increased concentration for many experiments have been produced. However, the increased concentration is not sufficiently high to enable us to investigate the physical properties of compounds of N^{15} particularly well. We should like to point out that modifications of our method may considerably increase the maximum concentration which can be secured. To accomplish this it is only necessary to use a fraction of the ammonia at the bottom of our column to feed another column of smaller diameter, a smaller hold-up, and a smaller rate of flow, in order to increase the concentration still further. The transport of this column would again depend upon the total flow in the column and the difference in concentration of the gas and liquid phases at the top of the column. Since the concentration of the material at the top of the second column would be $6\frac{1}{2}$ times higher, the difference in concentration would also be in-

[17] In the preliminary note which was based on Run 15, we reported a fractionation factor of 1.05 and 105 theoretical plates; this must be modified. We corrected the curve of Fig. 3 by eliminating the times apparently lost due to interruptions, giving a straight line or larger slope. In addition, two overhead samples gave us the large value of α, which on the basis of further work, was probably due to chance fluctuations in the rate of flow. Finally, an error in making the composite sample of the wash water gave too large transport. All these things gave consistent values for α and the number of theoretical plates.

creased by the same factor, and hence the total rate of flow could be decreased by a factor of $6\frac{1}{2}$ and yet maintain the same transport in the second column. This should, therefore, make possible a further increase in the concentration of N^{15} by a factor of $6\frac{1}{2}$ again if the second column were as efficient as the first. With smaller hold-up as would be expected for a smaller column, it should come to a steady state as rapidly as the first column, and hence the time required for the establishment of the maximum concentration should not be many times that required in our present experiments. Methods are being devised to carry out this extension of the method.

The transport when other apparatus, e.g. the Hertz type, is used, increases with the increased concentration of the starting material and hence our product can be used to advantage in such apparatus. The transport of a given apparatus using our product would be 6.5 times larger than when using natural nitrogen.

One of the disadvantages of the present method is the long time required for the apparatus to come to a steady state and the necessity of keeping it operating steadily during this time. One feature of our experiments is very encouraging in this connection. The interruptions which occurred during the course of our two most successful runs did not appreciably delay the time required for the establishment of the final steady state. A column of the rotating cone type does not drain if the rotor is stopped, and thus the distribution throughout the column is not changed if short shut-downs are required for repairs or to correct unavoidable accidents of the kind which we have encountered. This is a distinct advantage of this rotating type of column not present in the usual packed column which drains immediately if the process is interrupted, resulting in a mixing of most of the material throughout the column.

Previous experiments by Huffman and Urey on the distillation of water, led us to expect a much higher possible total rate of flow through the column than that we have been able to use. They used approximately 2 moles of total flow per minute in their most successful run, or 33 cc of liquid water per minute and secured 430 theoretical plates, while in these experiments we have been able to use only about 0.1 of a mole of ammonia per minute, or 15 cc of solution per minute and secured only 85 to 90 theoretical plates. The number of theoretical plates in a column must be determined by several factors. The rapidity of exchange of ammonia with the solution should increase the number of theoretical plates according to all experience. To accomplish this large surfaces are required. On the other hand, mixing processes such as back diffusion, or more probably turbulence in the gas, must occur which work against a large number of theoretical plates. It would appear that these mixing characteristics should be about the same in the case of the distillation of water and the exchange reactions which we have used here. Furthermore, the slow process in the exchange between the gas and the liquid phase would appear to be the rate with which mixing occurs in the liquid phase. We had anticipated that mixing would be as great in the liquid phase consisting of ammonium salt solutions, for example, as in the case of distillation of water. Such appears not to be the case. One would, of course, expect that ammonium ion would hardly diffuse as rapidly at ordinary room temperatures as water molecules at 60° to 70° as were used in the experiments of Huffman and Urey, but the difference could hardly be as great as that which we encountered.

Referring to Table III, we see from the values of k secured for Runs 9 and 11, that the number of theoretical plates is nearly the same when the exchange reaction $NH_3-(NH_4)_2SO_4$ is used as when NH_3-NH_4OH is used. Hence the difficulty can hardly be that the reaction of NH_3 dissolved in water to form NH_4^+ is slow for if this were the case the number of plates should be markedly less in Run 9 than in Run 11 which is not true. It appears to us that the slow process is probably at the interface. Either ammonia does not condense readily on the surface of water, i.e. the accommodation coefficient is low, or the liquid surface under our conditions has a relatively impervious film of foreign material. An oily film is present when the commercial ammonium sulfate is dissolved in water. The methyl alcohol was added to remove this as it did judging from superficial observation. Ten percent of ethyl alcohol was

tried in some experiments to see whether the operation was improved but there appeared to be no marked improvement.

It should be noted that it is not necessary for the large ammonium sulfate molecule to diffuse through the liquid phase and hence cause much slower rates of diffusion than in the case of water, since the mixing processes in our problem consist only in an ammonium ion being transported from one part of the liquid to another and its position taken by a second ammonium ion.

A comparison of the results of Run 9 and of Runs 15 and 16 leads us to believe that the use of the $NH_3-NH_4NO_3$ reaction would probably be more satisfactory for the concentration of N^{15} than that of $NH_3-(NH_4)_2SO_4$ reaction, if the corrosion difficulties can be eliminated.

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Evidence for Halogen Films on Tungsten in the Surface Ionization of Potassium Halides

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Molecular rays of the potassium halides were directed in high vacuum against tungsten and tungsten-oxygen surfaces, and the positive ion current to a collector cylinder was measured as a function of the surface temperature. Degrees of ionization on oxygen-free surfaces were calculated upon the assumption that each halide molecule produced one positive ion on striking a tungsten-oxygen surface. The high temperature results on oxygen-free filaments (1800°–2380°K) were interpreted as indicating surface dissociation of the potassium halide molecule, followed by partial ionization of the potassium atom and by the escape of the halogen as an atom. In the approximate temperature range 1800–1600°K a progressive change in the surface, with decreasing temperature, toward a higher work function was observed. This change led to surfaces of constant high work function, which were interpreted as due to the formation of halogen layers on the tungsten.

INTRODUCTION

THE surface ionization of the alkali metals on tungsten and tungsten-oxygen surfaces has been investigated by Ives,[1] Langmuir,[2] Becker,[3] Meyer,[4] and others,[5, 6] up to temperatures (about 1500°K) at which photoelectric currents become a complication in the type of ionization cell used by them. The range from 1500° to 2700°K was recently shown by two of the authors[7, 8] to be accessible to study by a molecular ray method. In this experiment a beam of potassium atoms of constant intensity passed in a high vacuum through a hole in a cylindrical metal shell and struck a tungsten wire at the center. The cylinder was maintained at a negative potential with respect to the wire. Part of the potassium atoms lost their electrons to the tungsten surface, evaporated as positive ions, and were discharged on striking the cylinder. This positive ion current, i_+, was measured as a function of the temperature of the wire. Then, without disturbing the beam, the wire was coated with a layer of oxygen and a larger, temperature-independent current was observed. This current (designated as i_{WO}) was assumed, following Langmuir and Kingdon,[2] to represent 100 percent ionization of the potassium atoms striking the wire. The number of unionized atoms, i_a, leaving the wire at each temperature was calculated from the relation, $i_a=i_{WO}-i_+$.

[1] Ives, Phys. Rev. **21**, 385 (1923).
[2] Langmuir and Kingdon, Proc. Roy. Soc. **107A**, 61 (1925).
[3] Becker, Phys. Rev. **28**, 341 (1926).
[4] Meyer, Ann. d. Physik (5) **4**, 357 (1930).
[5] Killian, Phys. Rev. **27**, 578 (1926).
[6] Morgulis, Physik. Zeits. Sowjetunion **5**, 221 (1934).
[7] Copley and Phipps, Phys. Rev. **48**, 960 (1935).
[8] Copley and Phipps, Phys. Rev. **45**, 344 (1934).

The data were treated by the Saha-Langmuir[2] equation,

$$\log_{10}\frac{i_+}{i_a}=\log_{10}\frac{\omega_+}{\omega_a}+\log_{10}\frac{1-r_+}{1-r_a}+\frac{(\Phi-I)\epsilon}{2.303kT}. \quad (1)$$

Here i_+/i_a is the equilibrium ion-atom ratio at zero field; ω_+/ω_a, the statistical weight ratio, ion to atom; r_+ and r_a, the reflection coefficients respectively of ion and atom from the surface; Φ, the work function of the surface at the temperature T; I, the ionization potential of the alkali atom; ϵ, k and T have their usual significances. ω_+/ω_a is $1/2$, and r_+ and r_a are presumably negligibly small.[9] If $\log_{10} i_+/i_a$ be plotted against $1/T$, the expected intercept on the axis of ordinates is $\log_{10} 1/2$ or -0.301. The observed value was -0.02. It has been suggested[10] that Φ has a temperature dependence of the form $\Phi=\Phi_0+\alpha T$ in the working range of temperature; in which case (1) would assume the form:

$$\log_{10}\frac{i_+}{i_a}=\log_{10}\tfrac{1}{2}+\frac{\alpha\epsilon}{2.303k}+\frac{(\Phi_0-I)\epsilon}{2.303kT}. \quad (2)$$

The value of α for tungsten as calculated from the observed intercept would be 5.6×10^{-5} volt-deg.$^{-1}$, and the value of Φ_0 would be 4.51 ($\pm$0.01) volt.

In 1930 Rodebush and Henry observed[11] that certain alkali halides are also ionized on tungsten-oxygen surfaces. They suggested that the salt molecule undergoes a preliminary dissociation on the surface into atoms, that the alkali atom then evaporates as an ion, and that the halogen leaves as an atom. The authors have investigated the behavior of the potassium halides on clean and on oxygen-coated tungsten as a function of temperature by a molecular ray method similar to that described above. A preliminary report of this work has appeared.[12]

Experimental

In Fig. 1 a quartz capsule A containing the salt and provided with a small opening B is surrounded by a nickel cylinder C; the latter is placed at the center of a closely wound tungsten spiral D which is provided with heavier glass-encased tungsten lead-out wires E. By the use of storage batteries to heat the spiral, the temperature of the salt is maintained sufficiently near to constancy for the needs of the experiment. A shutter F actuated from above by an electromagnet permits interruption of the beam at will. A small pin-hole G in the collector cylinder H serves to select a narrow beam of molecules, which strike the filament I. Those which miss the filament pass through the larger hole J on the opposite side and strike the glass wall, which is liquid-air cooled. The filament is a 5 cm length of 2 mil (0.005 cm diameter) aged tungsten wire held taut by a 6 mil (0.015 cm diameter) tungsten spring. Filament temperatures were determined as described in a previous communication.[7] The apparatus was enclosed in a jacket of Pyrex, 52 mm in diameter, which could be cracked off repeatedly with a hot wire and sealed back after each recharging of the quartz capsule with salt. Before a run was started the apparatus was surrounded by a furnace and baked out at 475–500°C for several hours. During a run the entire vessel was immersed in liquid air, but was not sealed off from the pumps. Protective liquid-air traps were employed. Electron emission measurements indicated a partial pressure of oxidizing gases of less than 10^{-10} mm of Hg. No ionization gauge tests were made of the total pressure. The magni-

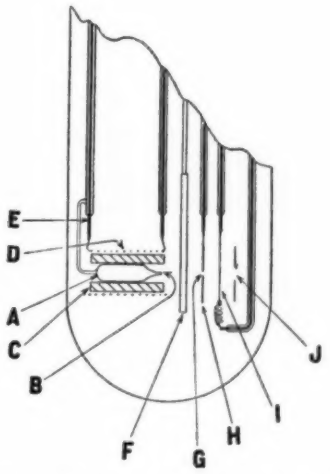

FIG. 1. Essential parts of the ionization chamber.

[9] Taylor and Langmuir, Phys. Rev. **44**, 423 (1933).
[10] Becker, Phys. Rev. **45**, 694 (1934).
[11] Rodebush and Henry, Phys. Rev. **39**, 386 (1932).
[12] Copley and Phipps, J. Chem. Phys. **3**, 594 (1935).

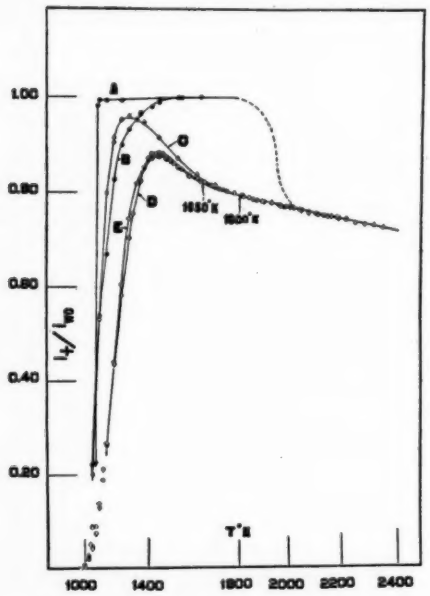

FIG. 2. Plot of i_+/i_{WO} (degree of ionization) against temperature. *A*, KI on W-O, ◒; *B*, KCl on W-O, ◓; *C*, KI on W, ⊙; *D*, KCl on W, ♀; *E*, KBr on W, -⊙. The dotted line indicates the stripping of the oxygen layer.

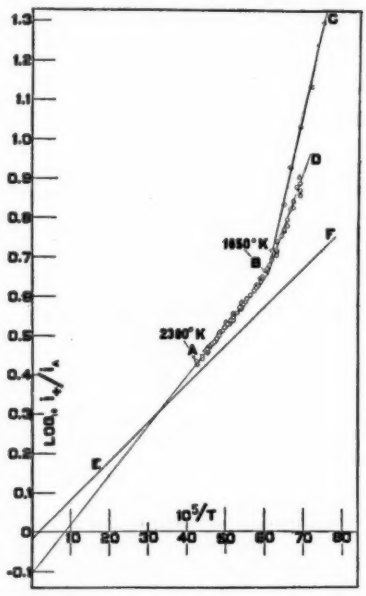

FIG. 3. Plot of $\log_{10}(i_+/i_a)_{E=3000}$ *versus* $10^5/T$. ♀=KCl; ⊙=KBr; -⊙=KI; *AB*, KCl, KBr and KI on W, Eq. (3); *BC*, KI on W-I, Eq. (6); *BD*, KCl (or KBr) on W-Cl (or W-Br), Eq. (7); *EF*, K on W, Eq. (5).

tude of the beams employed corresponded to a specific rate of arrival at the filament of approximately 4.3×10^{13} molecules-cm^{-2}-sec.$^{-1}$. To form the tungsten-oxygen surface small amounts of air were admitted by a fine capillary. This was always done at the end of a run, since the vacuum was found to deteriorate with repeated admissions of air. Further details of experimental procedure have been given in a previous paper.[7]

The potassium halides used in these experiments were Mallinckrodt's reagent quality chemicals. In each case the salt was fused in a platinum dish in air, powdered on a hot plate, transferred to the quartz capsule, and finally fused in the capsule.

RESULTS

Figure 2 shows the ratio i_+/i_{WO} plotted as ordinate against temperature as abscissa. The ratio i_+/i_{WO} may be considered as the degree of ionization of the impinging halide molecules on an oxygen-free surface, if we assume that on such a surface *part* of the salt molecules yield one potassium ion per molecule, and that on a W-O surface *every* salt molecule yields one ion. The shaded circles show the results for KCl and KI on a W-O surface. Although a complete curve for KBr on a W-O surface was not obtained, the existence of a shelf identical with the one for KCl and KI was definitely established. The dotted line shows the course of ionization during the stripping off of the oxygen layer in the range 1800° to 2000°K. The full circles show the results for KCl, KBr and KI on a tungsten surface free from oxygen. Onset of ionization for all species from both surfaces occurs at approximately 1000°K. It is seen that at temperatures above 1800°K the curves for the three salts merge, indicating that the ionization process is the same; but that from the onset of ionization up to 1800°K the curves show dissimilarities. KI shows a very pronounced maximum; KCl and KBr show slighter maxima which agree rather closely with each other.

Figure 3 is the plot of the logarithm of the ratio i_+/i_a against $1/T\times10^5$, for the data on oxygen-free surfaces, from the maxima up to the highest temperatures employed. i_a was calculated here as was done for the potassium metal case from the relation, $i_a=i_{WO}-i_+$. It is seen that in the approximate temperature interval 1800–1600°K a transition occurs to a steeper

slope, as the temperature decreases. The curve for KI rises more steeply than that for KCl and KBr. The heavy line *EF* shown in Fig. 3, the equation of which is given below in (5), represents the data which the authors obtained previously[7] for potassium metal on tungsten. It is to be noted that this line is less steep than that for the salts; also that it crosses the line for the salt data and has a smaller negative intercept upon the axis of ordinates.

Since the data for KCl, KBr and KI in the region *AB* were in agreement with one another within experimental error, the method of least squares was applied to the aggregate of points in this region, and the following equation was obtained:

$$\log_{10}\left(\frac{i_+}{i_a}\right)^{KX}_{E=3000} = \frac{1248(\pm 23)}{T} - 0.100(\pm 0.012). \quad (3)$$

This is for 45 volts on the collector cylinder (electric field at the surface of the wire of the order 3000 volt-cm^{-1}). A study of the effect of electric field at the surface of the wire upon the ion-atom ratio showed a slight increase in ionization efficiency with increasing field. When correction to zero field was made in the same way as was done for potassium metal,[7] the following equation was obtained:

$$\log_{10}\left(\frac{i_+}{i_a}\right)^{KX}_{E=0} = \frac{1120(\pm 50)}{T} - 0.09(\pm 0.02). \quad (4)$$

This equation is to be compared with that obtained[7] for potassium metal over approximately the same temperature interval; namely,

$$\log_{10}\left(\frac{i_+}{i_a}\right)^{K}_{E=0} = \frac{987.2(\pm 8.2)}{T} - 0.019(\pm 0.005). \quad (5)$$

Discussion of Results

In the general region *AB* (more exactly, from 1800° to 2380°K), since all three halides appear to have identical ionization curves, we are led to assume[13] that the ionization process is the same for all; namely, $K = K^+ + E^-$ on an essentially clean tungsten surface. Such an ionization process would presumably involve: (1) a surface dissociation of the halide molecule into atoms; (2) an ionization of the potassium atom; and (3) escape of the halogen atom after a life on the tungsten surface so short as to affect the work function of the surface only very slightly. On the basis of the above assumption, experimental Eq. (4) was compared with theoretical Eq. (2). The value of Φ_0 obtained from the slope was 4.54 ($\pm$0.01) volt. The interpretation of the intercept term is more uncertain. If one neglects reflection coefficients in the salt as in the metal case, the existence of a larger negative intercept for the salts than for the metal could be accounted for by assuming that the surface in the salt case, with its slightly higher work function (4.54 compared with 4.51 volt) had a smaller value of α (4.2×10^{-5} compared with 5.6×10^{-5} volt-degree^{-1}). Whether or not this be the correct interpretation, it is thought that the differences between the two curves are greater than can be accounted for by the experimental errors in the two cases. A further discussion of this point will be given in a later paragraph.

The low temperature regions (*BC* for KI and *BD* for KCl and KBr) are accounted for as follows. In this temperature range a complete W-X (X = halogen atom) layer analogous to the well-known W-O layer is formed, having a work function higher than that of a clean tungsten surface, and one characteristic of the halogen atom involved. On these W-X surfaces the surface dissociation of the impinging salt molecule into atoms occurs as on a clean tungsten surface, but the ionization of the potassium atoms proceeds more efficiently.

The equation for the line *BC*, which is interpreted as giving the course of the ionization when KI molecules strike a W-I surface, is

$$\log_{10}\left(\frac{i_+}{i_a}\right)^{KI}_{E=3000} = \frac{4780(\pm 470)}{T} - 2.25(\pm 0.32). \quad (6)$$

From the second member of this equation one calculates for $(\Phi_0)_{E=3000}$ of the W-I surface 5.27 ($\pm$0.10) volt. The equation for the line *BD*, which is interpreted as giving the course of the ionization when KCl molecules strike a W-Cl (or KBr molecules, a W-Br) surface, is

$$\log_{10}\left(\frac{i_+}{i_a}\right)^{KCl,\,KBr}_{E=3000} = \frac{2920(\pm 370)}{T} - 1.12(\pm 0.24). \quad (7)$$

[13] So far as the authors are aware, no mass-spectrographic study of this process has been made.

From the second member of this equation one calculates for $(\Phi_0)_{E=3000}$ of the W-Cl (or W-Br) surface 4.82 ($\pm$0.08) volt. A study of the effect of voltage upon ionization in the case of W-X surfaces is incomplete; preliminary observations indicated that the effect is small and of the same order of magnitude as that for clean tungsten.[7]

The interpretation of the large negative intercepts in Eqs. (6) and (7) is uncertain. However, in thermionic emission studies of surfaces covered with a layer of an electronegative gas a much larger value of the constant A in the Richardson equation than the theoretical (120 amp.-cm^{-2}-deg.$^{-2}$) is always observed.[14, 15] Large negative intercepts in the present experiment correspond to large values of A in thermionic emission measurements.

It is now possible to suggest a tentative explanation of the small differences observed between the slope and intercept obtained in the high temperature range for the salts and those obtained for potassium metal on tungsten. If we assume that a small but constant fraction of the tungsten surface holds adsorbed halogen atoms[16] even up to the highest temperatures, we should expect the work function of the surface in the salt case to be slightly higher than that of clean tungsten.

Conclusion

At temperatures below 1000°K (the onset of ionization, Fig. 2) we assume that KX molecules arriving at a tungsten surface orient to form a complete layer WXK of low work function, analogous to the layer WOK which has been investigated by Langmuir and Kingdon.[2] At about 1000°K a partial stripping of potassium begins, exposing patches, W-X, of high work function, on which ionization can occur. When the maximum of the ionization curve is reached we assume that stripping of the potassium atoms from the composite layer is complete, and that a complete W-X layer exists. This layer is stable through a range of temperature from the maximum (Fig. 2) to approximately 1600°K. Above this temperature the X atoms evaporate from a larger part of the surface. We assume, however, that in the high temperature range, where the salt curves appear to have merged, a constant small fraction of the surface holds on to halogen atoms.

In the case of oxygen-coated tungsten the present data give no suggestion as to the type of layer formed on the surface at temperatures between the onset of ionization and the shelf. At higher temperatures the existence of the shelf in the ionization curve is best explained by assuming surface dissociation of the salt molecules on the W-O surface, followed by complete ionization of the potassium atoms and evaporation of the halogen as atoms.

An attempt to study potassium fluoride led to inconclusive results. A surface of high work function was obtained which gave 100 percent ionization over a considerable range of temperature; but, owing to the hygroscopic character of KF, it was not certain whether this layer was a fluorine or an oxygen layer. It was noted, however, that the layer stripped at a lower temperature than does the oxygen layer. Further work is being directed toward nonhygroscopic alkali fluorides in order to decide this point.

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[14] L. A. Dubridge, Proc. Nat. Acad. **14**, 788 (1928).
[15] Dushman, Rev. Mod. Phys. **2**, 381 (1930).
[16] See for example the observation of Taylor and Langmuir (reference 9), that 0.5 percent of the surface of an aged tungsten filament held cesium atoms more firmly than the rest of the surface.

The Absorption Coefficient of Nitrogen Pentoxide in the Ultraviolet and the Visible Absorption Spectrum of NO_3

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Absorption spectrograms have been made of the gaseous system $N_2O_5-O_3$ during the decomposition of the ozone and into the subsequent decomposition of the N_2O_5, placing these in time such that one was taken when the system consisted essentially of only N_2O_5 and oxygen. From such spectrograms as the last mentioned, the absorption coefficient, α_{10}, of N_2O_5 has been measured over the wave-length range 3800–2850A. The value rises steadily from approximately 0.002 at the first wave-length to approximately 0.52 at 2850A. The absorption coefficient curve continues to rise to shorter wave-lengths and qualitative observations indicated no maximum as far as 2400A. No absorption which could be attributed to N_2O_5 could be observed in the 4500A region. Absorption spectrograms of NO_3 in the visible are given. In a study using low dispersion of the influence of oxygen on the absorption spectrum of NO_2, no noticeable effect was observed.

INTRODUCTION

IN the course of studies of the absorption spectra of the nitrogen oxides in progress in this laboratory, the authors have made observations on the system nitrogen pentoxide-ozone in the gas phase. In the presence of appreciable amounts of N_2O_5, ozone, even of low concentration, decomposes with a measurable rate at ordinary temperatures.[1] Over the period of its decomposition there exists in the mixture a higher oxide of nitrogen which is believed to be NO_3.[2] This decreases in concentration with the ozone, the concentration of the N_2O_5 remaining essentially constant. At the time of complete disappearance of the ozone, nitrogen pentoxide and oxygen alone are present. Following this, nitrogen dioxide makes its appearance as a product of the N_2O_5 decomposition which at ordinary temperatures also proceeds with a measurable rate. The thermal decomposition of N_2O_5 makes it difficult to introduce pure N_2O_5 alone into an absorption cell and to obtain absorption spectra[3] of the gas, without some NO_2 having made its appearance during these operations. Since NO_2 itself absorbs in the visible and ultraviolet, its presence is not desired while measuring the absorption of N_2O_5. Oxygen which is present at all times in such a mixture, possesses no interfering absorption.

In a suitable absorption cell containing originally nitrogen pentoxide and ozone there is thus the opportunity to observe both the absorption of the higher oxide when relatively large amounts of ozone are present, and the absorption of nitrogen pentoxide at that point in time when the ozone has completely decomposed and before nitrogen dioxide has yet made its appearance. Using a cylindrical absorption cell of 2 meters length to intensify the absorption of the NO_3 which is present at very low concentration, the authors have obtained photographs of the NO_3 spectrum, and have studied the absorption of nitrogen pentoxide, making quantitative measurements of the intensity of the latter over a range of wave-lengths in the ultraviolet, working at the above-mentioned point in time when the tube contained only nitrogen pentoxide and oxygen. In the course of the work observations were also made relative to the influence of oxygen on the absorption of NO_2.

EXPERIMENTAL

The 2 meter absorption cell, made of 3 cm diameter Pyrex tubing, was equipped with quartz windows attached through graded seals, and was made part of a closed system in which the gases were circulated by means of a water-cooled glass

[1] Tolman and White, J. Am. Chem. Soc. **47**, 1240 (1925); Nordberg, Science, **42**, 580 (1929); Schumacher and Sprenger, Zeits. f. physik. Chemie, **136**, 77 (1928); **B2**, 267 (1929); Sprenger, Zeits. f. Elektrochem. **37**, 674 (1931).

[2] Hautefeuille and Chappuis, Ann. de l'école norm. sup. series 2, **11**, 137 (1882); series 3, **1**, 103 (1884); Compt. rendus acad. sci. **92**, 80 (1881); **94**, 1111 (1882); Warburg and Leithäuser, Ann. d. Physik **20**, 743 (1906); **23**, 209 (1907); Schumacher and Sprenger, Zeits. f. angew. Chemie **42**, 697 (1929); Sprenger, Zeits. f. Elektrochem. **37**, 674 (1931).

[3] Urey, Dorsey and Rice, J. Am. Chem. Soc. **51**, 3190 (1929); Dutta and Sen Gupta, Proc. Roy. Soc. **A139**, 397 (1933).

plunger-type pump. The system, which was entirely of glass, consisted of the following elements in series, given in order and in the direction of the circulation of the gas mixture: the circulating pump, a water-cooled ozonizer of conventional form, a portion of glass tubing which could be heated by means of a resistance winding, two U-type traps, the absorption tube with an inlet and outlet tube at opposite ends, the system finally closing again at the circulating pump. The plunger or piston of the pump was operated magnetically by means of a surrounding solenoid, the current in which was varied periodically about 4 times per second by a multivibrator vacuum tube circuit. The latter was installed after mechanical interruption of the current had produced local radio disturbance. An all-glass pressure gauge of a twisted hollow ribbon type was used in reading pressures, its direct motion being amplified mechanically to the motion of a small mirror which threw a spot of light on a graduated scale after the manner of galvanometer practice.

The apparatus whose volume was approximately 1500 cc was filled with the desired amount of nitrogen pentoxide by first slowly admitting air to the evacuated system over liquid-air surfaces to remove water and carbon dioxide. By operating the ozonizer and condensing the resulting nitrogen oxides by means of one of the U-traps cooled in a dry-ice alcohol bath, an amount of nitrogen pentoxide, known roughly from the pressure drop, was collected. The remaining air was then pumped from the system with a Hyvac oil pump, and the system sealed. Oxygen was next admitted to a pressure of about 600 mm Hg through a break-off valve, and the system again sealed. With nitrogen pentoxide frozen out in the dry-ice alcohol trap, the oxygen constantly circulating in the system could be partially converted to ozone, after which the nitrogen pentoxide could be evaporated into this gas. Care was necessary here to evaporate in such a way as to distribute the N_2O_5 uniformly throughout the circulating gas. Nonuniformity of the distribution was a source of error in the work, and special effort was made to minimize this.

As soon as the evaporation was complete there existed the condition of highest NO_3 in the system, the tube being visually blue, due in a small measure to the absorption of ozone but chiefly to the absorption of NO_3. At this time satisfactory spectrograms could be had of the NO_3 spectrum. With time the NO_3 and ozone steadily decreased, the contents of the tube finally passing through a colorless stage, directly followed by the appearance of brown fumes of NO_2. It was at this point of absence of both ozone and NO_2 at which plates were taken to make a spectrophotometric determination of the intensity of absorption of N_2O_5 in the ultraviolet. After the N_2O_5 decomposition was complete, the system was in a stable condition, the nitrogen being in the form of NO_2 and N_2O_4. The system could be returned to the initial condition as often as desired by holding the $NO_2-N_2O_4$ mixture in one of the cold traps until sufficient ozone had been made by the ozonizer, and then carefully evaporating the oxides of nitrogen into the gas stream where they were converted by the ozone to N_2O_5. The N_2O_5 could then be frozen out and the oxygen strengthened in ozone content by reozonizing. Thus as many runs as desired could be made with a single filling of gas.

Results

A number of spectrograms were made of the absorption of NO_3, and since so far as the authors are aware no photograph of the spectrum has hitherto been published, a set of these are reproduced in Fig. 1. The first strip above the wave-length scale is the spectrum of the source, a tungsten filament lamp. The several strips above this are spectra taken consecutively, reading upward, as the N_2O_5 was evaporated from the cold trap into the circulating oxygen-ozone mixture as described above. In the second, third, and fourth strip (*a*, *b*, and *c* respectively) the strongest of the ozone bands can be noticed as broad absorption faintly overlying that of NO_3 which increases in this order. In the fifth strip (*d*) the evaporation is complete, the ozone has already been reduced somewhat, and the NO_3 is at its maximum concentration. The following strips show the decrease of NO_3 accompanying the decomposition of ozone, and in the last and top strip (*i*) finally the appearance of NO_2. These spectra were taken with a large Steinheil 3-prism glass spectrograph using an Eastman spectro-

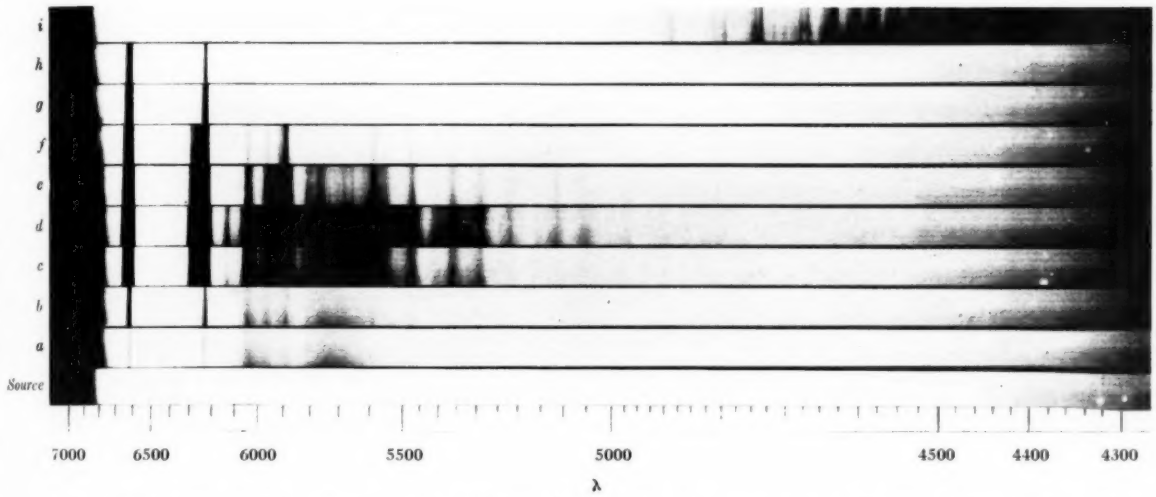

FIG. 1. The absorption of NO_3, overlain with weak ozone absorption in *a*, *b*, *c*. The absorption of NO_2 shows in *i*. The apparent relative intensity differences within the NO_3 spectrum between different strips is probably to be accounted for by the diffuse ozone absorption overlying certain of these. The wave-length, λ, is given in angstroms. Maximum N_2O_5 pressure roughly 80 mm Hg; maximum O_3 pressure roughly 50 mm Hg.

scopic I–F plate. The wave-length scale was constructed from neon and mercury lines which were also taken on the plates. As might be expected for the case of such a molecule, the absorption spectrum of NO_3 appears complicated. From the fine structure that appears at some points it would not be surprising if higher dispersion were to show considerably more detail as is the case with NO_2. All the prominent absorption maxima agree satisfactorily in position with those recorded by Warburg and Leithäuser, who state that their pictures were taken on a Rowland grating, but do not describe the grating further. Insofar as qualitative observations were made in the present work on the rate of the disappearance of ozone and NO_3, they are in accord with the results of Schumacher and Sprenger.[1] Sprenger[1] concludes from his kinetic measurements that with an N_2O_5 pressure of 20 mm Hg and an O_3 pressure of 100 mm Hg, the NO_3 pressure is about 0.02 mm Hg at 20°C. The quantitative light absorption measurements reported by Sprenger at two wave-lengths lead with this concentration to very high values of the absorption coefficient of NO_3 in the strongest of the absorption maxima. While not given in the ordinary form by Sprenger, from his data one finds a value of roughly $\alpha_{10}=500$ at the absorption maximum in the vicinity of 6650A, expressed in the conventional units, per cm of the pure gas at 0°C and one atmosphere. While high, this is probably not excessive for such a molecule composed of four atoms and possessing rather sharp narrow regions of absorption such as are evident in Fig. 1. The absorption is, however, somewhat unusual for an inorganic molecule at such long wave-lengths. An exploratory plate taken with the Eastman spectroscopic type *N* showed that absorption bands of NO_3 could be detected to approximately 7100A.

The spectrograms of the N_2O_5 absorption were taken on Eastman III–O plates using a Hilger E2 quartz spectrograph, working at the point mentioned above, when all ozone and NO_3 had disappeared and before NO_2 had begun to appear. The procedure consisted in taking a series of exposures throughout a time interval of which this point was approximately the middle. In this way the plates usually contained exposures still showing ozone absorption as well as exposures in which the ozone absorption had disappeared but the NO_2 absorption had made its appearance. Between these there usually existed, however, an exposure which was sufficiently free of either of these to be representative of the absorption of N_2O_5 alone. The extent to which this ideal condition was actually approached in the particular exposure chosen on each plate as the one upon which to make quantitative measurements, depended upon the care which had been exercised in

avoiding nonuniform distribution of the N_2O_5 during evaporation into the circulating oxygen-ozone mixture and in the proper placing of the exposure in time during the decomposition. Since ozone in small amounts does not absorb appreciably in the range 3300–3800A, and since NO_2 in small amounts does not absorb appreciably in the range 2800–3300A, it was realized that for measurements in the 2800–3300A region it was safer to lean slightly in the direction of being a little past the ideal point in the decomposition, while for the 3300–3800A region it was safer to use an exposure which if anything may have had a trace of ozone yet remaining.

On each of the plates a series of exposures was made for the purpose of plate calibration, using five screens of known transmission. These and the exposure chosen for the measurement of the N_2O_5 absorption were measured with a recording densitometer and the reduction of light intensity caused by the absorption of the N_2O_5 computed in the conventional way. The results of these measurements are shown in Fig. 2. They come from five different plates, two of which were taken at an N_2O_5 concentration of 98 mm Hg at room temperature, roughly 25°C. The open and closed circles in the figure lying at 3500A and above represent respectively the measurements of these two plates. The three other plates were taken at a pressure of 4.5 mm Hg and constitute the principal portion of the results, shown in Fig. 2 from 3500–2800A. The triangles and squares represent points determined by two somewhat different methods of measurement and are scattered among these three plates.

The determination of the higher pressure of nitrogen pentoxide was made by noting the pressure change upon the condensation and upon the evaporation of the solid and also by the pressure change during the N_2O_5 decomposition to $NO_2-N_2O_4$. As a result of these measurements the pressure was found to be 98 mm Hg at room temperature, which was taken as 25°C, and the value is probably good within ±5 percent.

The determination of the lower pressure of nitrogen pentoxide was made by three different methods: by noting the actual pressure change in the gas phase decomposition, making correction for the $NO_2-N_2O_4$ equilibrium in the resulting mixture; by observing the pressure change during the condensation of the $NO_2-N_2O_4$ mixture when all the oxide was in this form; and by determining the pressure change on either the condensation or evaporation of the N_2O_5 as such. Throughout these measurements at the low pressure correction was made for the influence of room temperature on the pressure of the gas in the cell and for the influence of changing barometric pressure on the readings of the pressure gauge with which the pressure measurements were made. The value 4.5 mm Hg was chosen as a result of these measurements, and is believed to be correct within ±5 percent.

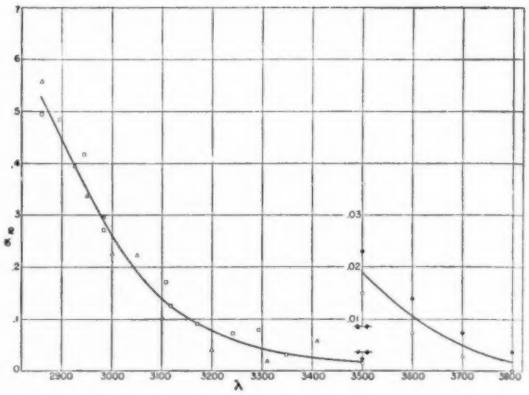

FIG. 2. Absorption coefficient of N_2O_5, α_{10}, given in the units per cm of pure gas at 0°C and one atmosphere and plotted against the wave-length, λ, in angstroms.

As seen in Fig. 2, continuous absorption due to N_2O_5 has been followed as far as 3800A. The only other substance in the present system which might lead to absorption at such long wave-lengths is NO_2, and as was remarked above, the effort was made to choose an exposure before the time when the system contained pure N_2O_5 and oxygen, in order to avoid the possibility of having NO_2 absorption present, even though some ozone absorption showed, since the ozone absorption does not extend with appreciable strength to such wave-lengths. To wave-lengths shorter than 2800A the intensity of absorption increases rapidly, and our qualitative observations disclosed no tendency for the absorption to pass through a maximum as far as 2400A.

Kondratiew and Polak[4] have reported that oxygen effected a change in the absorption spectra of NO_2 in the region of its first predissociation.

[4] Kondratiew and Polak, Zeits. f. Physik **76**, 386 (1932).

Later they[5] state that a further study of their plates, taken on a small grating spectrograph, did not substantiate their earlier findings. In the interim between the appearance of these two papers the present authors attempted a study of the effect of admitting oxygen to NO_2, and using a small glass Hilger spectrograph could detect no change in the absorption spectra of NO_2. Thus the negative results are in accord, though in view of the complicated structure of the NO_2 spectrum it might be unwise to conclude that under conditions of high resolution no effect would be found.

Discussion

As remarked above, the value of the absorption coefficient, as given by the measurements of Sprenger in the strongest of the absorption maxima of NO_3, is very high. It is interesting to consider whether there is any obvious reason for this very strong electronic transition at such long wave-lengths, and the resultant blue color, in the NO_3 molecule. The NO_3 absorption lies in much the same position as does the visible absorption of ozone[6] and the gross intensity distribution with wave-length in the two absorptions is very similar, but the transition in ozone is extremely weak. The material in the NO_3 spectrum also appears much sharper than the diffuse bands of O_3. It does not seem reasonable to imagine any connection between the two spectra, since the three oxygen atoms in NO_3 will certainly not be ozone-like. The oxide N_2O_3 or a polymer of this is deep blue in the liquid state, as is well known. This absorption in the red was not however observed by Melvin and Wulf[7] in the path lengths which they used in studying gaseous N_2O_3, and it may be that the color is actually due to a higher polymer. One is reminded also of the intense blue color frequently characteristic of monomeric organic nitroso compounds[8] although it is not evident that there exists an analogous structure in the molecule NO_3. Since the molecule NO_3 contains an odd number of electrons, the general fact that it is highly colored is not surprising.

In the present work the continuous absorption of nitrogen pentoxide has been observed to somewhat longer wave-lengths than in the work either of Urey, Dorsey and Rice[3] or Dutta and Sen Gupta.[3] In agreement with the work of the former, we have not found the other absorption reported by Dutta and Sen Gupta at longer wave-lengths in the vicinity of 4500–4000A, this in spite of the fact that our effective path lengths were sufficient to follow the main continuous absorption to considerably longer wave-lengths than was the case in either of these two other researches. The nature of the dissociation process corresponding to this continuous absorption is, of course, not surely known, but if we compute the heat of dissociation of nitrogen pentoxide into N_2O_4 and normal oxygen atom, using the data given by Bichowsky and Rossini,[9] we find

$$N_2O_5 = N_2O_4 + O(^3P_2) - 61{,}160 \text{ cal.}$$

which corresponds to a wave-length of closely 4660A or about 2.65 volts. There is still a wide margin between the wave-length at which the absorption has been observed and that corresponding to the above process, and hence this process may indeed represent the actual dissociation. It seems probable that the continuous absorption could be observed still further to the red in longer paths than we have employed, as is frequently the case in dealing with continuous absorption of this character. It is notoriously difficult to fix the beginning of such absorption. An excited oxygen atom would not be an admissible product, apparently, since the first excited state $O(^1D_2)$ is about 2 volts or 45,000 calories higher, which would place the beginning of dissociation corresponding to this process at about 2800A.

[5] Kondratiew and Polak, Physik. Zeits. Sowjetunion **4**, 766 (1933).
[6] Wulf, Proc. Nat. Acad. **6**, 507 (1930).
[7] Melvin and Wulf, J. Chem. Phys. **3**, 755 (1935).
[8] See, for example, Baly and Desch, J. Chem. Soc. **93**, 1747 (1908).
[9] *Thermochemistry of Chemical Substances*, (Rheinhold Publ. Corp., 1936).

Spectral Sensitivity and Light Absorption of Dye-Sensitized Photographic Emulsions*

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Direct measurements on emulsions sensitized with certain cyanine dyes show a correspondence between the shapes of the light absorption and sensitivity curves in the region of color sensitizing. It was found that the absorption curves of silver bromide dyed with some cyanine dyes are essentially the same as the absorption curves of the dyes in saturated inorganic salt solutions. It is postulated that there are two types of adsorption of cyanine dyes to silver bromide, aggregated and molecular. An emulsion sensitized with a cyanine dye under proper conditions can show sensitivity in different spectral regions, corresponding to the light absorption characteristics of dye adsorbed in the aggregated and molecular states.

A CONSIDERABLE literature has been developed concerning optical sensitizing of photographic emulsions by dyes and the relationship between the light absorption of the emulsion and the spectral distribution of sensitivity. Reviews of the status of this question have been given by Bokinik[1] and Rabinovitch,[2] Mecke,[3] and Eggert[4] have briefly discussed the problem but were able to arrive at no definite conclusions because of the lack of experimental data.

One isolated experiment on the relation between light absorption and sensitivity has been reported. Eder[5] qualitatively determined the absorption of a silver bromide emulsion sensitized with eosin and found that the region of maximum light absorption coincided with the region of maximum sensitivity.

It is clear that light must be absorbed by the dyed halide of a sensitized emulsion before the latter can be photosensitive, but it is not necessarily true that sensitivity will exist at all wavelengths where absorption occurs. It is one purpose of this communication to present data which establish a direct correspondence between the shape of the light absorption curve of emulsions sensitized with certain dyes and the spectral sensitivity of the emulsions.

A second question of importance in optical sensitizing is that of the state of the dye when adsorbed to silver halide. No definite, direct experimental evidence dealing with this question appears to have been reported. There are data in the literature[6–11] on the molecular states of sensitizing dyes and their light-absorption characteristics in various solvents. Sheppard[6] observed systematic variations in the absorption curves of some cyanine dyes with changing solvent, and found that aqueous solutions were generally different in absorption characteristics from nonaqueous solutions. As the result of another study, Sheppard[7] concluded that certain cyanine dyes in aqueous media exist as colloidal aggregates, and that the absorption spectra of the colloids are different from those of dyes in true solutions. Bloch and Hamer[8] and Jelley[11] observed in some cases that an aqueous salt solution of a cyanine dye exhibited markedly different absorption properties from those of a methanol solution of the same dye.

Scheibe and co-workers[12] and Jelley[11] have recently reported studies on the aggregation of a cyanine dye, *N*, *N'*-diethylpseudocyanine chloride, in aqueous solutions. Scheibe and co-workers have established that not only does this dye change its state of aggregation in aqueous media, but that it is adsorbed to certain inorganic

* Communication No. 642 from the Kodak Research Laboratories.

[1] J. I. Bokinik, Kino-Photo Industry, **3**, 84 (1933).
[2] A. J. Rabinovitch, Acta Phys.-Chim. U. S. S. R., **2–3**, 369 (1935).
[3] R. Mecke, Trans. Faraday Soc. **27**, 370 (1931).
[4] J. Eggert, Trans. Faraday Soc. **27**, 386 (1931).
[5] J. M. Eder, Phot. Korr. **23**, 146, 574 (1886).
[6] S. E. Sheppard, Phot. J. **32**, 300 (1908).
[7] S. E. Sheppard, Proc. Roy. Soc. **82A**, 256 (1909).
[8] O. Bloch and F. M. Hamer, Phot. J. **59**, 21 (1928).
[9] S. E. Sheppard and H. Crouch, J. Phys. Chem. **32**, 751 (1928).
[10] G. Scheibe, Angew. Chem. **49**, 563 (1936).
[11] E. E. Jelley, Nature **138**, 1009 (1936); ibid. **139**, 631 (1937).
[12] G. Scheibe, L. Kandler, and H. Ecker, Naturwissenschaften **25**, 75 (1937). This note contains references to earlier papers.

materials in a state corresponding to that in the aqueous system. They report shifts in absorption spectra corresponding to this change.

The results of the present investigation were obtained prior to the publication of the work of Scheibe, and establish that changes in state of certain cyanine dyes occur in aqueous media. It has been found that this change can most easily be produced by adding certain inorganic salts to the aqueous system. The present investigation has led to the observation that the light-absorption characteristics of silver bromide, to which certain cyanine dyes have been adsorbed, are essentially the same as those exhibited by the dyes in an aqueous salt solution. These results are in agreement with those of Scheibe *et al.* for dyes adsorbed to glass, quartz, etc. They indicate that the dye adsorbed to silver bromide is frequently in a state of aggregation similar to, if not identical with, that exhibited in aqueous salt solutions.

In the following experiments, much of the work has been done with microcrystals of silver halide as found in photographic emulsions. These emulsion "grains" formed in gelatin solution have been used for several reasons. First, data obtained can be applied directly to the problem of the elementary photographic process. Secondly, the surface of the silver halide is more accurately reproducible in this form. Experiments made with gelatin-free silver halide have established that gelatin has little effect on the light-absorption properties of sensitizing dyes adsorbed to silver halide.

The sensitizers used were cyanines. Attention has been confined to these dyes because of their general superiority for photosensitization when compared with acid dyes, such as erythrosin.

Experimental

The work here reported was facilitated by the use of the automatic spectrophotometer designed and developed by Hardy.[13] The percentages of light reflected at any wave-length were directly measured over the region 4000A–7000A with this instrument; for qualitative purposes this reflection curve may be taken as the inverse of the absorption curve. The spectral distribution of photographic sensitivity of the emulsions was qualitatively determined by exposure through a neutral optical wedge in front of a transmission grating.[14] The effect of energy distribution in the source has been calculated and found to produce negligible differences between the apparent and true maxima of sensitivity.

In some experiments, reflection measurements were made on sensitized emulsions coated and dried on glass plates; the emulsions contained about 4 grams of silver bromide and 6 grams of gelatin per 100 cc, and usually 2 mg of dye dissolved in 5 cc of methanol were added just before coating. In other experiments the dye was added to the emulsion, the grains were removed by centrifuging, taken up in a little water, and then pipetted onto glass plates and allowed to dry before spectral analysis.

Reflection curves were run on samples of pure silver bromide dyed from water solutions, and also on samples of pure silver bromide dyed from methanol. In both cases 4 grams of thoroughly washed silver bromide in 100 cc of water or methanol and 2 mg of dye were used; in the case of dye adsorption from alcohol, the bromide was washed several times with methanol before addition of dye. The bromide was separated either by settling or by centrifuging and was coated on glass plates for analysis. In several cases, the separated, dyed silver bromide was taken up in a small quantity of 3 percent gelatin solution, placed on glass plates and allowed to dry before the determination of its spectral reflection.

Several experiments were made with pure silver iodide and pure silver chloride. The amounts of dye and of silver halide used were approximately the same as those in the bromide experiments.

In one series of experiments the silver-ion concentration of a bromide emulsion was varied between 10^{-3} and 10^{-10} molar by adding silver nitrate or potassium bromide solutions before addition of the dye. The grains were separated by centrifuging and their spectral reflection determined. In another series, the *p*H of the emulsion was adjusted to values between 5.75 and 9.85, and the absorption characteristics of the emulsion grains were measured. In a third

[13] A. C. Hardy, J. Opt. Soc. Am. **18**, 96 (1929).

[14] L. A. Jones, *Photographic Sensitometry*, second edition (Eastman Kodak Co., 1934), p. 144.

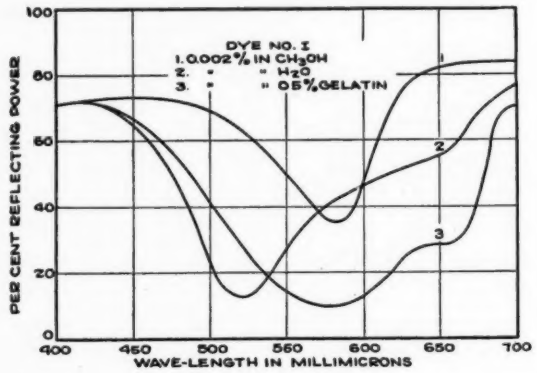


FIG. 1.

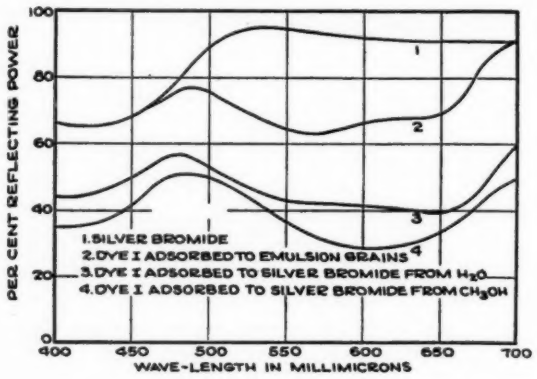

1. SILVER BROMIDE
2. DYE I ADSORBED TO EMULSION GRAINS
3. DYE I ADSORBED TO SILVER BROMIDE FROM H_2O
4. DYE I ADSORBED TO SILVER BROMIDE FROM CH_3OH
PER CENT REFLECTING POWER
WAVE-LENGTH IN MILLIMICRONS

FIG. 2.

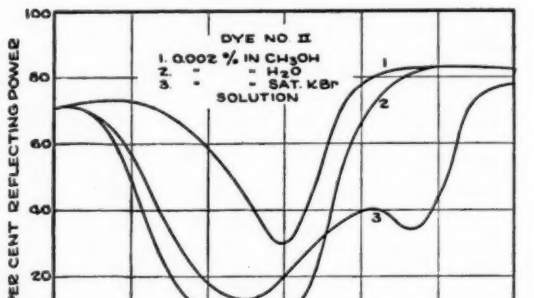


FIG. 3.

series, the amount of dye added to 100 cc of emulsion was varied between ½ mg and 10 mg and the reflection of the grains measured. The measurements of silver-ion and hydrogen-ion concentration were made by using a silver bromide and glass electrode, respectively, in an electrical system employing a condenser and ballistic galvanometer.

In all of the experiments, the completeness of adsorption was estimated from the color of the gelatin solution, water, or alcohol from which the silver salts had been separated. In almost all cases there was no perceptible color in the liquid medium. Mention will be made in cases where adsorption was not complete, otherwise it is understood that substantially all of the dye was taken up by the silver halide.

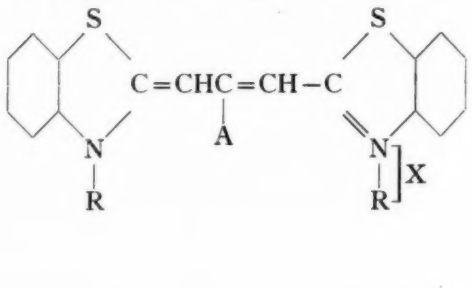
During the spectral analysis there was occasionally slight fading of the dye and darkening of the halide. It was therefore necessary to change the position of the sample two or three times during a single analysis. The fading and darkening effects were thus reduced but not completely obviated. For this reason the reflection curves at the regions of minimum reflection (maximum absorption) are slightly flattened. This effect does not alter the general shape of the absorption curve, and the error involved does not seem important for the purposes of the experiments.

The absorption spectra of the sensitizing dyes in methanol and in aqueous solutions were determined by the automatic spectrophotometer. It was found that during measurement with the usual spectrophotometers, bleaching of the dye was excessive. The concentration of dye in the solutions was 0.002 percent. The amount of inorganic salt, usually potassium bromide, when added to the aqueous solutions of dye, was determined by the individual dye. In general, solid halide was added until a point of incipient dye precipitation was reached. In some cases the solutions became slightly turbid. Absorption measurements were made on these aqueous systems without further treatment.

More complete information about individual experiments is given below.

EXPERIMENTAL RESULTS

The dyes used in this investigation are thiacarbocyanines of the general formula:



in the cases of dyes I, II, IV, and VI, in which R is an alkyl group, A a hydrogen or an alkyl group, and X a halide ion. Several of these dyes are substituted in the nucleus. Dye III is a thia-pseudo- (or 2′-) cyanine, and V a pseudo- (or 2,2′-) cyanine.

The properties and preparation of the various sensitizers used have been described in the literature.[15–19]

Typical dyes of known photographic properties were chosen for investigation, and from their study it is felt that a broader viewpoint may be obtained concerning the mechanism of sensitizing by cyanine dyes. The dyes used in this investigation were kindly supplied by Dr. L. G. S. Brooker and Mr. F. L. White of these Laboratories.

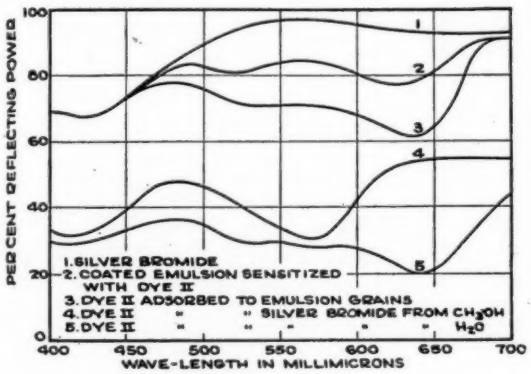

PER CENT REFLECTING POWER
WAVE-LENGTH IN MILLIMICRONS
1. SILVER BROMIDE
2. COATED EMULSION SENSITIZED WITH DYE II
3. DYE II ADSORBED TO EMULSION GRAINS
4. DYE II " " SILVER BROMIDE FROM CH_3OH
5. DYE II " " " " " H_2O

FIG. 4.

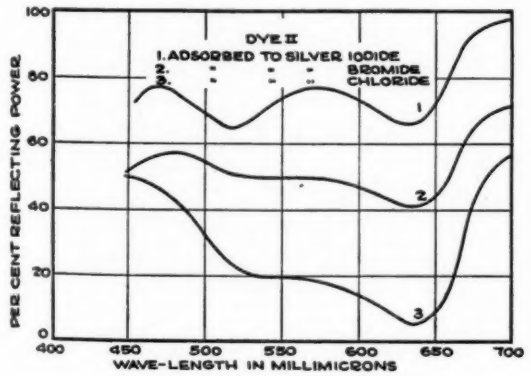


FIG. 5.

[15] L. G. S. Brooker and F. L. White, J. Am. Chem. Soc. 57, 547 (1935).
[16] L. G. S. Brooker and F. L. White, J. Am. Chem. Soc. 57, 2480 (1935).
[17] F. M. Hamer, J. Chem. Soc. 206 (1928).
[18] L. G. S. Brooker and G. H. Keyes, J. Am. Chem. Soc. 57, 2488 (1935).
[19] F. M. Hamer, J. Chem. Soc. 3160 (1928).

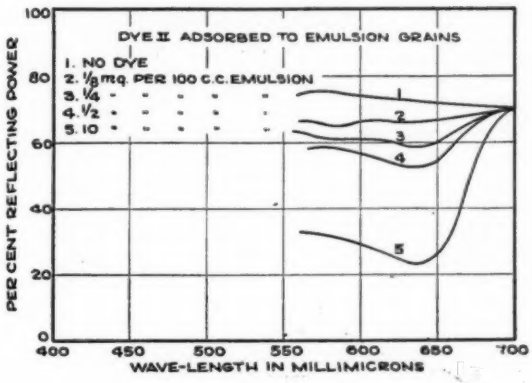

DYE II ADSORBED TO EMULSION GRAINS
1. NO DYE
2. 1/8 mg. PER 100 C.C. EMULSION
3. 1/4 " " " "
4. 1/2 " " " "
5. 1 " " " "
PER CENT REFLECTING POWER
WAVE-LENGTH IN MILLIMICRONS

FIG. 6.

The results of a number of experiments on the absorption characteristics of several dyes under a variety of experimental conditions are presented in Figs. 1, 2, 3, 4, 5, 6, and 7. The ordinates in these figures represent either the reflecting power of the solid samples or the transmission of the dye in various solutions. As stated earlier, the absolute value of the reflection at any wave-length is not significant, but the relative reflection values in any curve are sufficiently accurate to give a very fair qualitative determination of its shape. The curves in some of the figures are deliberately spaced to avoid intersection, but their respective shapes are maintained.

It can be seen in Fig. 1 that the absorption curves of dye I in water, in methanol, and in aqueous gelatin, are strikingly different. The absorption behavior of dye II under similar conditions is shown in Fig. 3. The addition of gelatin solutions to an aqueous solution of dye II does not produce a change in absorption spectrum, as is the case with dye I, but the introduc-

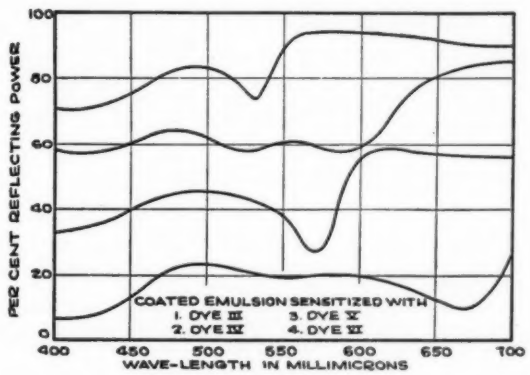


FIG. 7.

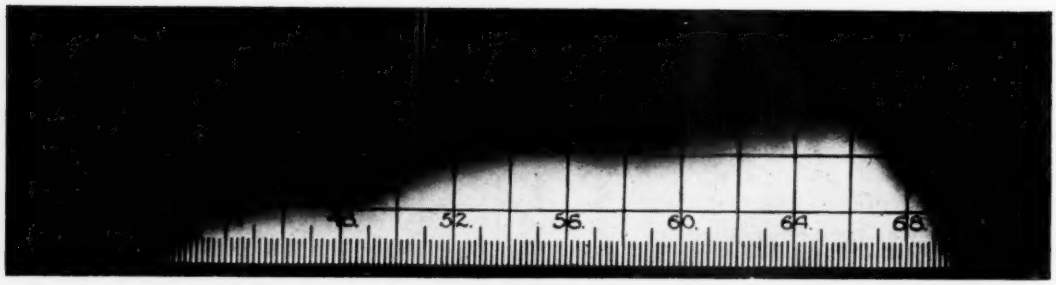


FIG. 8.

FIG. 9.

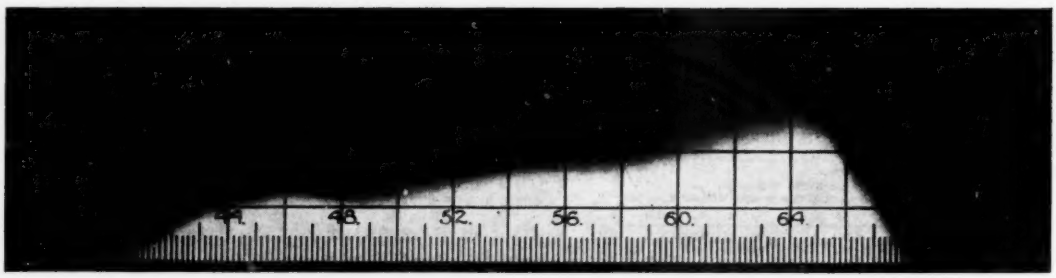


FIG. 10.

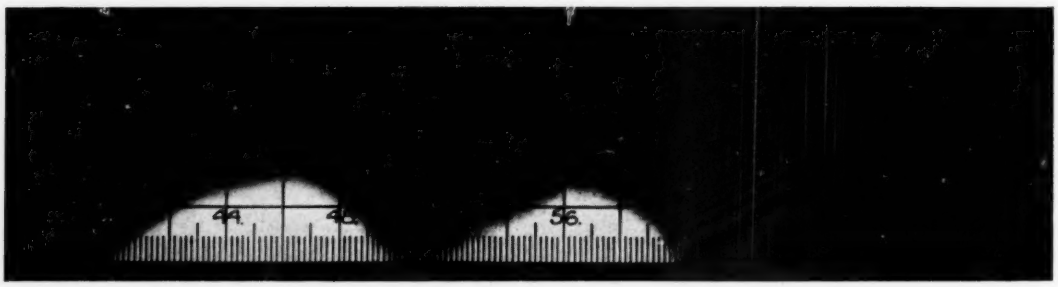


FIG. 11.

tion of solid potassium bromide caused the shift, as shown in Fig. 3. With some dyes, due to salting out, the aggregated state could not be obtained. The saturation of aqueous solutions of dye II with the following salts resulted in an absorption curve like that observed in saturated potassium bromide: sodium carbonate, potassium carbonate, potassium nitrate, sodium chloride, and sodium thiocyanate. The following salts were without effect: calcium acetate, sodium acetate, sodium sulfate, sodium oxalate, and sodium sulfite.

In Fig. 2 are shown the reflection curves for dye I adsorbed to emulsion grains, to pure silver bromide and to pure silver bromide when dyed from methanol solution. The reflection curve of

FIG. 12.

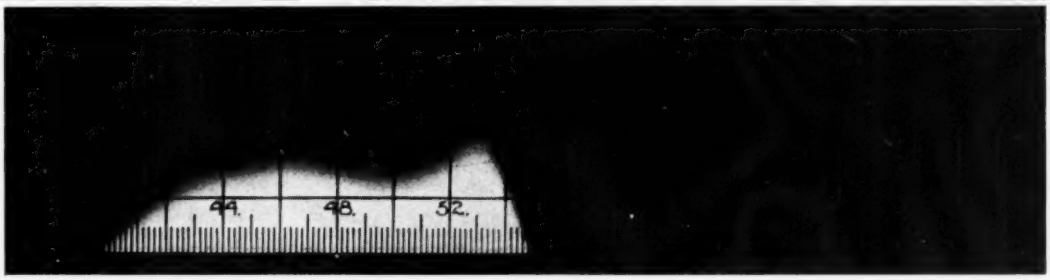


FIG. 13.

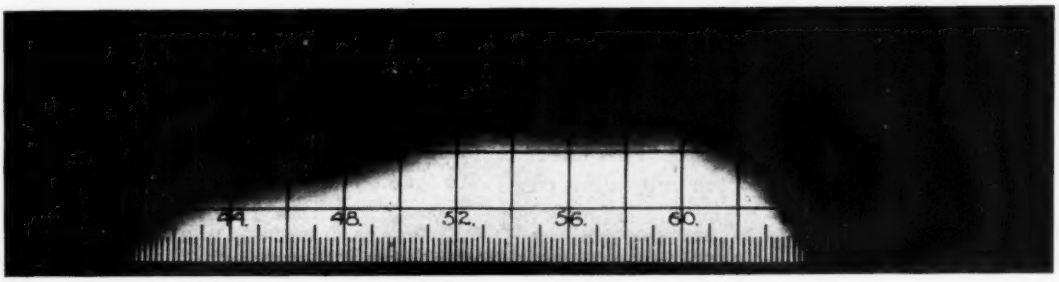


FIG. 14.

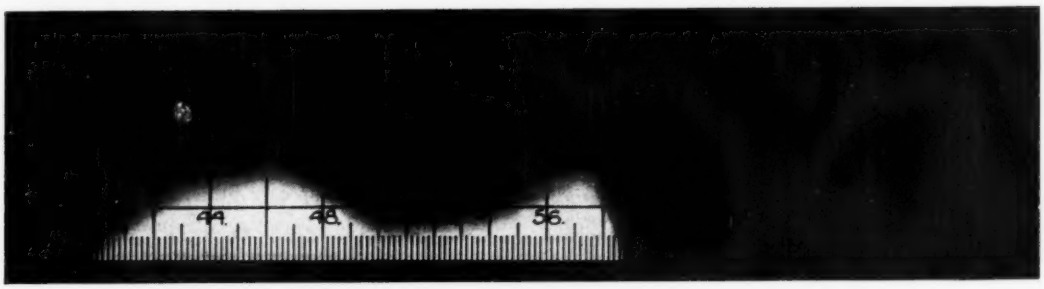


FIG. 15.

silver bromide dyed from water is independent of gelatin and is different from the curve of silver bromide dyed from methanol. Fig. 4 presents similar curves for dye II and also a curve of a normally coated photographic emulsion sensitized with this dye. It is seen from Fig. 4 that dye II adsorbed to silver bromide from water exhibits a reflection curve which is independent of the presence of gelatin. The absorption curve of dye II adsorbed to silver bromide from methanol solution is markedly different from the curve of the dye adsorbed to the bromide from water.

Figure 5 shows reflection curves of dye II adsorbed from water to silver iodide, silver bromide, and silver chloride. The curve of silver

iodide dyed with dye II from methyl alcohol is identical with that of silver bromide dyed from the same solvent.

In Fig. 6 are found the reflection curves of an emulsion sensitized with various quantities of dye II. The quantities used were $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$, and 10 mg of dye per 100 cc of emulsion, respectively. It is significant that not only does the amount of light absorption decrease with decreasing dye concentration, but that the shape of the curve also changes. At the lowest dye concentration, the absorption maximum at 6350A has vanished, and a new maximum at 5750A has appeared. This maximum is in the same position as the maximum of the curve shown by silver bromide dyed with dye II from methanol. This effect is frequently observed, but there are many cases where the position of the maximum changes but little with concentration.

In Fig. 7 are given the reflection curves of normally coated, dried emulsions, sensitized with dyes III, IV, V, and VI, respectively. In each case 1 mg of dye was added to 100 cc of emulsion before coating.

The shape of the reflection (or absorption) curve of bromide emulsion grains dyed with dye II was found to be independent of the silver-ion concentration over the range of 10^{-3} to 10^{-10} molar. The dye was completely adsorbed at a silver-ion concentration lower than 10^{-7}, but incompletely at concentrations greater than 10^{-6}. This breaking point occurs at a silver-ion concentration equal to that of the solubility of silver bromide. At a silver-ion concentration of 5×10^{-3} molar, no dye was adsorbed. In general, the higher the silver-ion concentration, the smaller was the amount of dye adsorbed to the grains.

Table I.

Figure	Dye	Concentration (mg/100 cc emul.)	Compare with Figure
8	I	5.0	2, curve 3 1, curve 3
9	I	0.02	2, curve 4
10	II	4.0	4, curve 3 3, curve 3
11	II	0.1	4, curve 4
12	III	1.0	7, curve 1
13	IV	1.0	7, curve 2
14	V	1.0	7, curve 3
15	VI	1.0	8, curve 4

Table II. *Wave-lengths of absorption maxima given in A.U.*

State of Dye	Dye IV	Dye III
CH_3OH soln.	5500	4800
H_2O soln.	5500	4800
Saturated KBr soln.	5150; 2nd max. 6150	4800; 2nd max. 5300
Adsorbed to AgBr:		
from H_2O	5900; 2nd max. 5200	5350
from CH_3OH	5700	5150
from 1% gelatin	5900; 2nd max. 5200	5350

It was found that the shape of the reflection curve of emulsion sensitized with dye II was independent of *p*H in the range studied, 5.75 to 9.85.

Some qualitative observations were made. If dye II is adsorbed to silver bromide from water in the absence of gelatin, the absorption curve of the wet, dyed bromide is that given in Fig. 4, curve 5. If the sample is allowed to dry, the shape of the absorption curve changes to that of silver bromide dyed from methyl alcohol solution. The original color is restored if the bromide is moistened with water. If silver bromide is dyed from water, the grains separated and then moistened with a 3 percent gelatin solution, the curve is that of Fig. 4, curve 5. Upon air drying, the shape of the absorption curve of the grains does not change. The small amount of gelatin present prevents the change in state upon drying.

Silver bromide was dyed from water, the grains separated by settling and methyl alcohol added. The color of the grains changed to that characteristic of halide dyed from methanol. During the change of color, no dye appeared to leave the grains and go into the alcohol; the change apparently occurred at the surface of the bromide. By decanting the alcohol and adding water to the settled grains, the original color was restored. The system is therefore reversible.

The behavior just described for dye II adsorbed to silver bromide is not specific. Dye I also may be made to change its absorption properties by drying, wetting with water, wetting with alcohol, etc.

Figures 8 to 15 are the spectrograms of normally coated emulsions sensitized as described in Table I. In Table I, the fourth column

TABLE III. *Wave-lengths of sensitivity maxima given in A.U.*

DYE	HIGH CONCENTRATION	LOW CONCENTRATION
IV	5900	5700
III	5300	5200

lists the absorption curves of the sensitized emulsions with which the spectrograms should be compared. For dyes I and II, two spectrograms corresponding to two different concentrations of dye are given. This will be discussed later.

The qualitative agreement between the absorption (by reflectance measurement) curves of the dye adsorbed on silver bromide and the spectral distribution of sensitivities of the various sensitized emulsions is very good. Any differences are easily within the experimental error.

Absorption (by reflectance) and sensitivity measurements have been made on about one hundred sensitized emulsions, and in no case has any disagreement been found between the shape of the absorption curve of the emulsion and the spectral distribution of sensitivity.

The absorption curves of dyes III and IV, dissolved in alcohol, water, and saturated potassium bromide, were determined, as well as their reflection curves when adsorbed to silver bromide from water and methanol. The results may be seen in Table II.

In Table III are given the maxima of spectral sensitivity.

DISCUSSION

The experimental results establish for the dyes investigated the qualitative correspondence between the light absorption of a sensitized emulsion and the spectral sensitivity distribution. This correspondence appears to hold not only for the positions of the maxima and minima of the absorption and sensitivity curves, but also for the relative strengths of absorption and sensitivity in the spectral region where light is absorbed by the dye. No correlations have been found which allow the prediction of the sensitivity of an emulsion sensitized with a dye when compared with the unsensitized emulsion.

The discussion of the fact that some cyanine dyes sensitize silver halide emulsions to wavelengths several hundred angström units longer than those at which light is absorbed in nonaqueous solvents resolves itself, in view of the present results, into the consideration of the causes for the unpredictable shift in the light absorption of the dye in methanol to that observed when the dye is adsorbed to silver halide. The experiments on the light absorption of some of these dyes in nonalcoholic media provide an insight to this phenomenon.

The observations of other workers[6–12, 20] have established that some cyanine dyes are aggregated in aqueous media. Scheibe and co-workers[12] consider this phenomenon to be due to a polymerization of dye molecules. Jelley,[11] however, has shown for the dye used by Scheibe in his investigation that the state is very probably not a polymeric one, but that the dye takes the form of a one-dimensional (nematic) crystal. His crystallographic evidence for this conclusion is supplemented by observations on the fluorescence behavior of the dye in saturated aqueous salt solutions. The question as to the exact states of cyanine dyes in aqueous media must await further detailed studies by these investigators.

Bloch and Hamer[8] have presented absorption curves of a number of different cyanine dyes in methanol and water. For almost all of these dyes the curves are very similar in the two solvents, and the dyes are therefore probably in the same state. On the other hand, the curves of Figs. 1 and 3 show that dyes I and II are not in the same state in water and methanol. Table I presents evidence that dye IV is in different states in alcohol and water, whereas dye III is in the same state.

The addition of certain salts, typified by potassium bromide, to aqueous solutions of dye II causes a definite change in the state of aggregation of the dye. The fact that nonhalide salts are capable of modifying the state of a halide containing dye is an indication that this change is not primarily due to some electrolytic dissociation effect, since there is no common ion. It is of even greater significance that the addition of a dilute gelatin solution alone can modify the state of dye I. In view of the contradictory evidence as to the exact state of cyanine dyes in aqueous systems, the arbitrary term "aggre-

[20] B. H. Carroll and D. Hubbard, Nat. Bur. Stand. J. Research 9, 529 (1932).

gated" will be used hereafter to designate the state of a dye in an aqueous medium characterized by an absorption spectrum essentially different from that of the dye in alcohol. As indicated by the absorption measurements, there are several degrees of aggregation possible for a given dye. Dyes I and II are different in water and in alcohol. For each of these dyes there is a third state which is definitely identified by sharp absorption maxima. Any system of dye, water, and salt may include a variety of states, dissociated and undissociated. The absorption curve of such a system is probably made up of several individual curves, each characteristic of a single species. The absorption coefficients of the several absorption maxima will be determined by the relative amounts of the various absorbing species, and consequently may vary within wide limits. It is not felt that with the present information further speculation is warranted.

A comparison of curve 3 of Fig. 1 with curve 2 of Fig. 2, and of curve 3 of Fig. 3 with curve 2 of Fig. 4, shows the striking similarity between the light-absorption curves of dyes I and II in an aggregated state, and of the same dyes when adsorbed to silver bromide from water or gelatin. There is a similar correspondence for dye III, as shown in Table II, but for dye IV the absorption curves of associated dye and of dyed silver bromide are not identical.

The agreement shown between the absorption maxima of dye in the aggregated state and adsorbed to silver bromide leads to the conclusion that the state of the dye is the same in the two cases. It is therefore consistent to term as "aggregated adsorption" the taking up of dye by silver bromide under conditions which give light-absorption curves similar to those of aggregated dye. In connection with this arbitrary definition, reference is made to the work of Sheppard and Crouch[9] who considered the possibility of adsorption of a colloidal type for the cyanine dye, Orthochrom T. These authors concluded that this dye was more probably adsorbed in a molecular-ionic condition.

With dye IV there is not exact agreement between the absorption curves of aggregated dye and dye adsorbed to silver bromide. The conditions under which association to form a definite aggregate occurs are probably the balance of a number of factors. It is not surprising that conditions have not been found which reproduce accurately the state of the adsorbed dye. The significant fact is that in several cases excellent agreement between the absorption curves of the dye in the aggregated and in the adsorbed state has been observed.

In Fig. 6 are shown the absorption curves of dye II adsorbed to silver bromide emulsion grains, the ratio of dye to silver varying by a factor of 80. At the lowest concentration of dye, the absorption maximum is at 5800A. In the higher concentration, the dye exhibits maxima at 6400A and 5800A. In the highest concentration, there is a single maximum at 6400A. It is evident that the state of the adsorbed dye has changed with concentration. At high concentration, adsorption is probably aggregated. At the lowest concentration, the dye is adsorbed in some other form. It may be postulated that this latter is characteristic of dye adsorbed in the molecular (unassociated) state.

In Figs. 2 and 4 are given reflection curves of dye adsorbed to silver bromide from methanol solution. These curves are strikingly different from those of the dyes adsorbed from water. Sheppard[6] has shown that in methanol, cyanine dyes are probably in true solution. Any dye adsorbed to silver halide from this solvent is therefore in equilibrium with a molecular rather than with an associated species. It is therefore reasonable to conclude that dye adsorbed to silver halide from methanol solution is in a non-aggregated or molecular form.

From Fig. 4, curve 4, and Fig. 6, curve 2, it is seen that the absorption curve of dye II adsorbed from gelatin solution at very low concentration is, within the precision of measurement, the same as that of dye adsorbed from methanol at high dye concentration. This is consistent with the concept of molecular adsorption, since it might be expected that dye in very low concentration would be adsorbed from gelatin in the molecular or nonaggregated state. It has been found that dye II which has been brought into the aggregated form by addition of potassium bromide to an aqueous solution can be transformed into the state existing in methanol solution by diluting with water.

The change in distribution of spectral sensi-

tivity of emulsions when using large and small quantities of dye is entirely consistent with the change in absorption. This is shown when Fig. 6, curve 2, is compared with Fig. 10, and Fig. 6, curve 5, with Fig. 11. That emulsion sensitized with a very low concentration of dye is similar in light-absorption characteristics to silver bromide dyed from methanol is shown by comparing Fig. 4, curve 4, with Fig. 6, curve 2.

For all of the cyanine dyes which have been studied, the sensitivity curve of emulsion sensitized with a low dye concentration is similar to the light-absorption curve of silver bromide dyed from a methanol solution of the sensitizer.

The change of the color of silver bromide dyed from water upon drying corresponds to a change of dye from aggregated to molecular form. As has been pointed out, this change is reversible. There are two plausible explanations for this behavior. The first of these is that the absorbing species are an electrolytically dissociated aggregated electrolyte and its nondissociated form. Upon drying, the dissociated form ceases to exist. Moistening will cause dissociation with consequent change in color. The fact that very small amounts of gelatin prevent the change from the dissociated to nondissociated form may be due to prevention of complete desiccation by the gelatin.

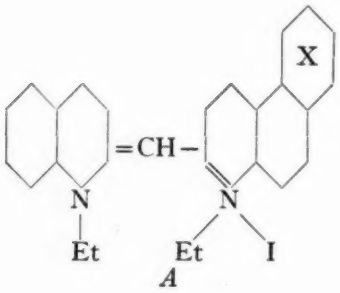
The second explanation of the reversible color of dyed silver bromide is that of aggregated and molecular adsorption. Upon drying silver bromide dyed from water, the forces (possibly those due to water dipoles) which tend to maintain the aggregated state are weakened or destroyed, and the individual dye molecules wander over the surface of the bromide until they form a uniformly distributed molecularly adsorbed layer. Moistening restores the forces which cause aggregation, and the molecules rearrange themselves to give the stable, associated form. The effect of gelatin in preventing change of color may be due to its adsorption at the unoccupied spaces on the bromide surface. Since the surface is then saturated with adsorbed material, there is no place to which the dye can wander, and hence forces much weaker than usual are capable of retaining the dye in its aggregated form. Furthermore, the thin coating of dry gelatin might offer considerable resistance to wandering of dye molecules over the surface.

The idea of dissociated and nondissociated forms of colloidal dye is not favored for several reasons. First, the amount of gelatin which is necessary to prevent change of color upon drying is extremely small, and the amount of water retained upon air drying is also very low. Secondly, an attempt was made to cover the surface of a fresh silver bromide precipitate as completely as possible by dyeing it from water with as much of dye II as would be adsorbed. This quantity was ten times that normally used in the other experiments. Upon air drying for five days, there was a slight regression of the maximum at 6400A, but there was by no means a complete change of color indicative of transformation to the molecular form. Presumably, the bromide surface was so completely covered with aggregated dye that even when dry the molecules could not wander to form a uniform molecular layer. This second observation cannot be explained on the basis of dissociated and nondissociated forms.

There is insufficient evidence at this time to afford a detailed picture of the state of the adsorbed dye. There is, however, a further observation of interest. It is that the halide ion is responsible for the adsorption of the cyanine dyes to silver halides. Many experiments have been made on the adsorption to insoluble compounds of some of the dyes here described. The dyes have been found to be adsorbed to the insoluble halides of lead, mercury[I] and copper[I]. They are not adsorbed to the insoluble carbonate, oxalate, or phosphate of silver, nor to lead sulfate or oxalate. When adsorption from water occurs, the light absorption of the dyed material is like that of dyed silver halide. The light absorption of salts dyed from methanol solution is similar to the absorption of the dye adsorbed to silver halide from methanol. The above facts indicate strongly that the light absorption of dyed silver halide is characteristic of the dye and halide ion, and is independent of the silver ion.

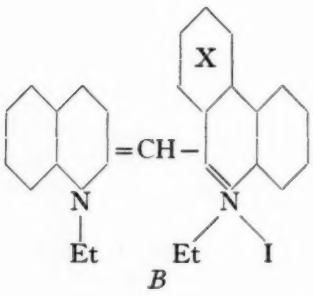
Another observation should be presented. The following isomers were supplied by Dr. L. G. S. Brooker and Mr. G. H. Keyes[21] of these Laboratories:

[21] L. G. S. Brooker and G. H. Keyes, J. Am. Chem. Soc. **58**, 659 (1936).

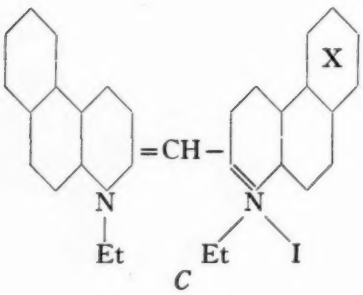


A

and



B



C

and

D

Dyes *A* and *C* sensitize photographic emulsions, while dyes *B* and *D* do not. Emulsion grains were dyed with each of the compounds: *A*, *B*, *C*, and *D*, and it was found that the dye was strongly adsorbed in each case. The gelatin was removed by centrifuging, and the reflection curves of the grains determined. The curves of all four dyes showed pronounced absorption maxima.

A probable explanation of the difference in sensitizing characteristics of the isomers is that the phenyl groups, *X*, in dyes *B* and *D* interfere with the proper exchange of energy between dye and silver halide, because of some steric effect in the molecule. Whether this inhibition of energy exchange is due to improper orientation of adsorbed dye at the bromide surface or to interference with collisions suitable for such exchange cannot be decided. The facts indicate that for photosensitization, not only is adsorption of dye to silver halide necessary, but also accessibility of the light-absorbing group to the silver bromide crystal.

The question of the mechanism by which energy is transferred from the light-absorbing dye-silver halide complex to the silver bromide crystal has been discussed. Bokinik[1] in particular has presented the views of various investigators. No discussion will be given at this point of the abundant speculation on this question. Recent developments in the theory of crystals, as applied to the photographic elementary act, have been presented by Webb.[22] It is felt that a theory of optical photosensitization should be compatible with this or a similar interpretation.

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[22] J. H. Webb, J. Opt. Soc. Am. **26**, 368 (1936).

Quantitative Relationships Between Light Absorption and Spectral Sensitivity of Dye-Sensitized Photographic Emulsions*

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Eastman Kodak Company, Rochester, New York
(Received July 23, 1937)

Quantitative measurements of light absorption and photographic sensitivity for orthochromatic and panchromatic films over the wave-length region λ4000–7000 have been made. The results show excellent correspondence between light absorption of the dyed silver bromide emulsion and its sensitivity over the entire wave-length region for the panchromatic film. For equal absorption, the orthochromatic film is less sensitive in the green than in the blue. It is concluded for the panchromatic sensitizing, that transfer of energy from the dye to the silver halide is very efficient. Possible mechanisms of the sensitizing process are discussed.

IT has recently been shown[1] that for photographic emulsions sensitized with certain cyanine dyes there is a qualitative correspondence between the shapes of the light-absorption curves of the dyed silver bromide emulsion and the spectral distribution of photographic sensitivity. It is of interest to ascertain the quantitative relationship between such absorption and sensitivity as a means of affording a direct measure of the efficiency of certain cyanine dyes as energy acceptors for latent-image formation. This study may also be used to determine if latent-image formation in a sensitized emulsion proceeds through the same mechanism in the two distinct wave-length regions: one, where light is absorbed by the silver halide, and the other by the dye or dye halide complex.

There are many data in the literature on the sensitivities of emulsions at various wave-lengths, some of the more accurate work being that of Jones and Sandvik.[2] No recorded data have been found on the light-absorption characteristics of a photographic material for which the spectral sensitivity distribution has been measured. This communication presents such absorption and sensitivity data for two commercial photographic emulsions.

The light absorption of the film in the spectral region λ4000A–7000A was determined by use of the improved automatic spectrophotometer designed by Hardy.[3] The light transmitted and reflected by the films in diffuse illumination was measured. From these data the percentages of light absorbed at the various wave-lengths were calculated. These absorption figures are accurate to within 5 percent. The sensitivities of the films for given wave-lengths were kindly determined by Dr. J. H. Webb and Mr. C. Evans of this Laboratory using a monochromatic sensitometer employing a double monochromatizing system as designed by Jones and Sandvik.[2] The precision of measurement varied between 2 and 10 percent, depending upon the wave-length region. The precision was least for the shortest wave-lengths. The calibration of the sensitometer in absolute energy units is accurate to within 25 percent.

Figure 1 presents the experimental results of the measurements on a high speed panchromatic emulsion coated on clear film base. The abscissas are in angstrom units. The ordinates give the percentages of light absorbed by the emulsions and also the reciprocals of the energies in ergs necessary to produce a density of one, on development for 4 minutes at 65°F in D-19 developer. This arbitrary measure of sensitivity has been selected as most satisfactory for the present purpose.

In any attempts to correlate the sensitivity of an emulsion with its light absorption, it is necessary to calculate the absorption characteristics of the individual silver bromo-iodide grains, since the absorptions of the coated emulsion for various wave-lengths are not pro-

* Communication No. 643 from the Kodak Research Laboratories.

[1] J. A. Leermakers, B. H. Carroll, and C. J. Staud (Communication No. 642 of this series), J. Chem. Phys. **5**, 878 (1937).

[2] L. A. Jones and O. Sandvik, J. Opt. Soc. Am. **12**, 401 (1926).

[3] A. C. Hardy, J. Opt. Soc. Am. **25**, 305 (1935).

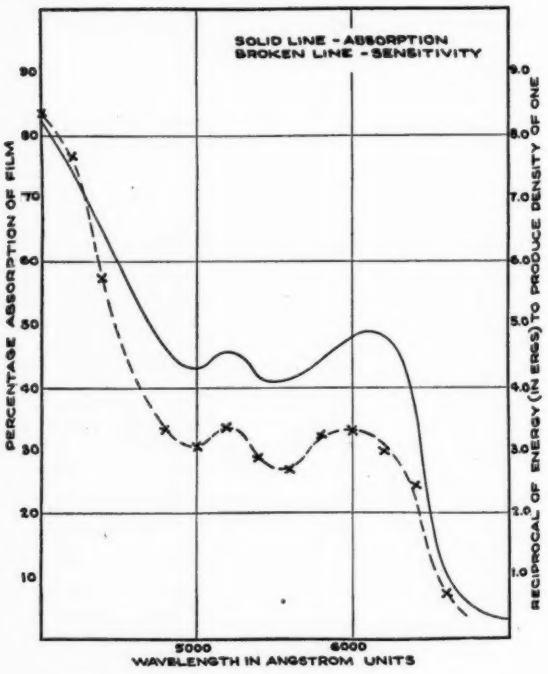
SOLID LINE - ABSORPTION
BROKEN LINE - SENSITIVITY
PERCENTAGE ABSORPTION OF FILM
RECIPROCAL OF ENERGY (IN ERGS) TO PRODUCE DENSITY OF ONE
WAVELENGTH IN ANGSTROM UNITS
5000
6000

FIG. 1.

portional to those of the single crystals. In calculating the absorption of the individual grain, it is assumed that Lambert's law holds for this system. This law is:

$$\log I/I_0 = -\alpha l,$$

where I/I_0 is the fraction of light transmitted, α is a constant, and l, the distance traversed by the light through the absorbing medium. The photographic emulsion is a heterogeneous system comprising dyed silver halide crystals and gelatin. The gelatin is transparent to light of the wave-lengths used, and may be neglected. The assumption that Lambert's law holds for the absorption of light by the silver halide is equivalent to considering each dyed emulsion grain to act as a unit of absorption thickness, and that these units are all similar. Internal reflections within the coated emulsion influence the absorption behavior to some extent, but since comparisons of absorption at different wave-lengths are to be made for the same emulsion, it is believed that Lambert's law will probably hold sufficiently well for the purpose.

The silver content per unit area and the size frequency characteristics of the emulsion being known, it is estimated that light passing through the film must traverse approximately 10 dyed silver halide crystals. An error of 100 percent in this estimate will not produce excessive error in the calculation of the relative absorptions because the absorption is a logarithmic function of the thickness. The figure 10 was used in the calculations. That this number of absorbing layers is approximately correct was verified by calculations from the absorption at λ4000A, using the known absorption coefficient for silver bromide.

In Fig. 2 the percentage absorption of the individual grain at λ4000A has been taken as unity, and the absorptions at the other wave-lengths are expressed as fractions thereof. Included in Fig. 2 is the curve for the sensitivity of the same emulsion relative to its sensitivity at λ4000A.

In Fig. 3 are the relative absorption and sensitivity curves for a high speed orthochromatic emulsion coated on clear film base. The experimental data were treated exactly as those for the panchromatic emulsion previously described.

The parallelism between the relative absorption and sensitivity curves for the panchromatic emulsion appears striking. The differences between the sensitivity and absorption maxima in the red are within experimental error. The data indicate definitely that for this emulsion the sensitivity as measured is directly proportional to the amount of light absorbed. It has been established by direct measurements that the sensitizing dyes used in these emulsions do not contribute appreciable absorption to the dyed silver halide grain at λ4000A. It may be concluded, therefore, that for this emulsion proportionality between absorption and sensitivity holds for spectral regions where the light is absorbed by the silver halide alone, and where it is absorbed only by the adsorbed dye or dye-silver halide complex.

The curves of Fig. 3 for the high speed orthochromatic emulsion show a general parallelism in that the positions of the sensitivity and absorption maxima coincide. There is, however, definitely greater sensitivity for light absorbed at λ4000A by silver halide than for light absorbed by the dye.

Several conclusions can be drawn from the results of the experiments with the panchromatic emulsion. First, with certain dyes under suitable conditions of sensitizing, the dye can act as an extremely efficient light acceptor for latent-image formation. The energy absorbed by the dye is transferred to the silver halide in such a manner that the latter is activated as efficiently as if it had been the absorber. Secondly, the mechanism of latent-image formation is independent of how the energy is absorbed, by the silver halide or by the dye. The latter conclusion may also be deduced from sensitizing and desensitizing studies by Sheppard,[4] and by Carroll and Hubbard,[5] and also from investigations[6] of the temperature coefficient of sensitivity of dye-sensitized emulsions.

The experiment with panchromatic emulsion indicates a close relationship between the sensitivity in ergs and the absorption. It might be expected that correlation should be between the number of quanta absorbed and the sensitivity.

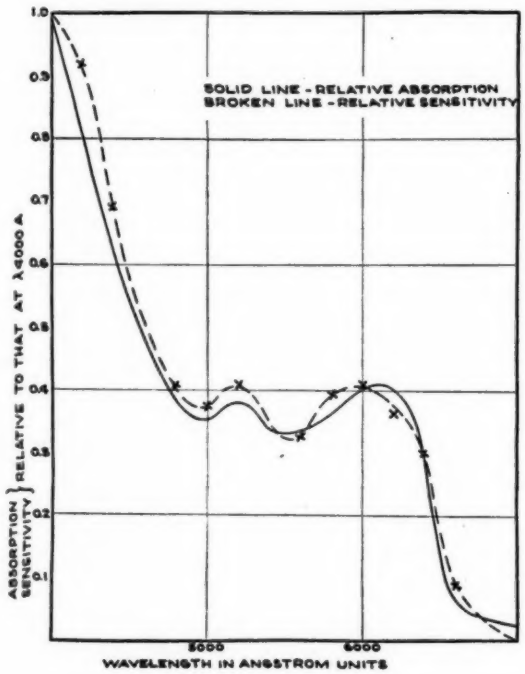

FIG. 2.

[4] S. E. Sheppard, Colloidal Symposium Monograph, **3**, 1 (1925).

[5] B. H. Carroll and D. Hubbard, Nat. Bur. Stand. J. Research **9**, 529 (1932).

[6] S. E. Sheppard, E. P. Wightman, and R. F. Quirk, J. Phys. Chem. **38**, 817 (1934).

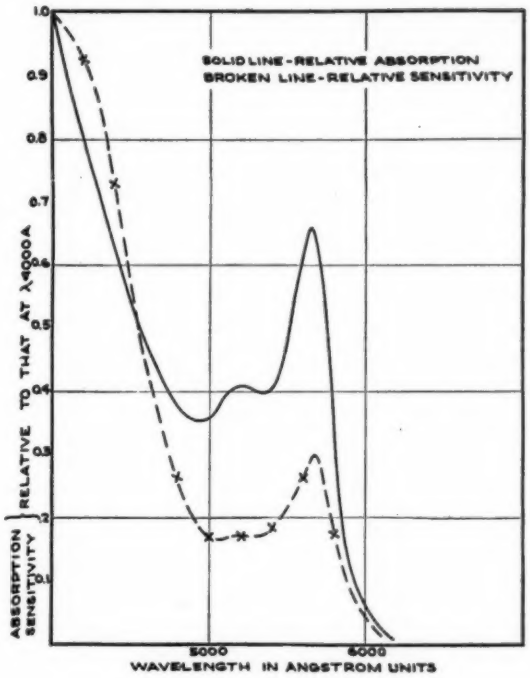

FIG. 3.

Unfortunately, the complexity of the system comprised of crystals varying in size and also slightly in iodide content seems to preclude the possibility of definitely deciding whether the sensitivity is determined by the number of quanta or by the number of ergs absorbed. There is evidence in the literature[7] that the smaller grains, which are those least sensitive inherently, are the most efficiently color sensitized. This would mean that the larger grains contribute relatively more blue speed, as measured at a density of 1.0, and that, consequently, a true sensitivity curve for dyed crystals of silver bromide of uniform size would exhibit greater speed in the red than is indicated in the curve for the entire emulsion. Greater red sensitivity would be consistent with a mechanism which involves quanta and not ergs.

A possibility not definitely excluded, but which it is felt is remote, is that a silver bromide emulsion grain becomes developable only after a certain amount of total energy has been added to the crystal, this energy being required to cause a rearrangement of the lattice forces in some

[7] S. D. Threadgold, Proc. IXth International Congress Photography, Paris, 418 (1935).

favorable way. This mechanism would require a correlation between sensitivity in ergs and absorption.

There are several possible mechanisms by which energy absorbed by the dye can be transferred to the silver halide so that the latter is made developable. The dye and silver halide may form a stable complex which acts as a unit, so that activation of dye and silver halide occur simultaneously. The fact that certain sensitizing dyes sometimes exhibit absorption curves in environments not containing silver halide which are very similar to the curves of dye adsorbed to silver halide[1] indicate that the latter is not involved in the primary absorption act. That is, excitation of the halide occurs subsequent to light absorption.

Another possibility of activation of the halide involves a mechanism similar to that of collisions of the second kind. In a collision of the second kind, energy absorbed by one species is transferred to a second on collision, any excess above that necessary for the activation of the latter being dissipated in the form of translational kinetic energy. In the present case, energy absorbed by the dye (independent of the silver halide) may be passed to the silver halide, the excess above that necessary to activate the halide going into vibrational excitation of the atoms of the crystal. The actual mechanism of energy transfer is obscure. No sharp distinction can be drawn between transfers of energy by molecular collision and transfers within a stable complex (such as dye-silver halide), inasmuch as during a true collision involving exchange of electronic energy there must occur some transitory complex formation. The use of the word "collision" in the present case appears objectionable. All that is necessary is that the dye pass its absorbed energy to the silver halide before deactivation by fluorescence or some other means. It is known[8] that complex organic molecules have relatively long lives (of the order of 10^{-7} seconds) in their activated states. It is possible that in the present case there may be a definite time lapse between activation of the dye and leakage of its energy through the potential barrier at the surface of the halide. This view is consistent with the facts known at present. There is evidence[9] that the function of a sensitizing dye is simply to pass on energy to the silver halide, and that this transfer does not involve destruction of the dye. Further, experiments by the author have shown that there is strong fluorescence of certain cyanine sensitizing dyes when adsorbed to silver halide. This fluorescence behavior is entirely consistent with the idea of a long-lived activated dye molecule which may pass on its absorbed energy to the silver halide or liberate it by other means.

A third mechanism of photosensitization requires the giving of an electron from the dye to the silver halide. Experiments on the photoconductivities of some cyanine dyes[10] indicate that photo-ionization takes place in regions of strong absorption. If it be true that the sensitizing dye is not destroyed during the activation of the silver halide, it is difficult to understand the mechanism by which the electron returns to the dye.

The author is inclined to the view that light energy is absorbed by the dye and transferred to the halide by some mechanism which may involve a type of collision or leakage through a potential barrier at the halide surface.

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[8] J. Franck and K. Herzfeld, J. Phys. Chem. **41**, 97 (1937).

[9] J. I. Bokinik and Z. A. Iljina, Acta Phys.-Chim., U. S. S. R. **2–3**, 383 (1935).

[10] N. Zchodro, J. Chim. Phys. **26**, 59 (1929).

Surface-Dye Concentration Relationships in Sensitized Photographic Emulsions*

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(Received August 23, 1935)

A study has been made of the relationship between the total surface of silver halide in a photographic emulsion and the concentration of sensitizing dye necessary to produce maximum sensitizing. It was found that the amount of dye producing maximum sensitizing is directly proportional to the silver halide surface. Approximate calculations indicate that at optimum sensitizing concentration, the sensitizing dye is adsorbed to the silver halide grains in a monomolecular layer.

IN the optical sensitizing of photographic emulsions by dyes, the photographic sensitivity conferred is dependent among other factors upon the dye concentration in the emulsion. The sensitivity increases with increasing dye concentration until a point is reached, beyond which definite decreases in sensitivity result. One important variable in the relation between dye concentration and photographic sensitivity is the total surface of the silver halide.

There are in the literature reports of two adsorption studies for two cyanine dyes[1, 2] and some acid dyes,[3] but no definite correlation is shown between the grain surface area and the dye concentration necessary to produce a given sensitizing effect, which the dyes in question are capable of producing.

This communication presents the results of a study of the surface-dye concentration relationships for seven emulsions and for three dyes. For all of the emulsions used, size frequency measurements were available. From these measurements, the total surface per cubic centimeter of emulsion was readily obtained.

The dyes used in the present investigation were cyanines.

To determine the effect of dye concentration upon photographic sensitivity as a function of the total surface of the silver halide grains, an extended series of emulsion coatings was made for each dye in each emulsion. Each series included coatings of the same emulsion sensitized with varying amounts of dye, in some cases a 250-fold range of dye concentration being investigated. The coated plates were exposed on an Eastman IIb sensitometer supplied with strips of standard Wratten tricolor filters, Nos. 25, 58, and 49, and processed according to the conditions most suitable for the particular emulsion. H and D curves were plotted for the sensitivities in the blue, green, and red spectral regions, and from these curves the inertia speeds and the contrasts (γ) were obtained.

In Figs. 1 and 2 are presented the results of a typical concentration study. The H and D speed and gamma for the three spectral regions are plotted against the logarithm of the dye concentration. It is seen in Fig. 1 that the sensitivities in the red and green spectral regions increase with increasing quantity of dye added to the emulsion until a definite maximum speed is reached. Greater quantities of dye result in marked decreases in sensitivity. The blue speed remains practically constant until the optimum dye concentration is exceeded, after which marked decreases in sensitivity result. The contrast changes are parallel to those of the speed changes, as seen in Fig. 2. For some dyes the concentrations giving maximum speed are almost the same as those for maximum contrast. For other dyes, or other emulsions, it is sometimes found that the contrasts decrease at a concentration of dye slightly lower than that which produces maximum sensitivity.

Curves similar to those of Figs. 1 and 2 have been constructed, and the concentration of dye producing maximum sensitivity has been determined for each combination of dye and

* Communication No. 644 from the Kodak Research Labor. tories.

[1] S. E. Sheppard and H. Crouch, J. Phys. Chem. **32**, 751 (1928).

[2] S. E. Sheppard, R. H. Lambert and R. L. Keenan, J. Phys. Chem. **36**, 174 (1932).

[3] A. J. Rabinovitch and K. C. Bagdassarjan, Kino-Photo Res. Inst. Moscow **3**, 5 (1935).

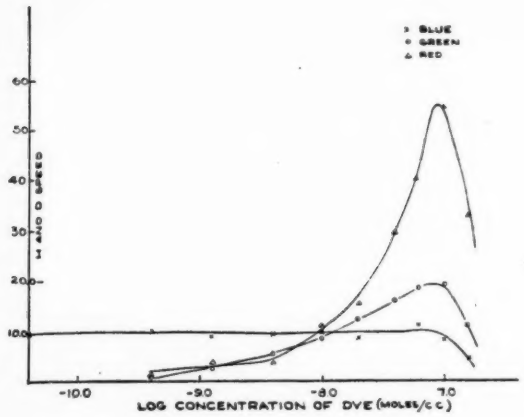

FIG. 1.

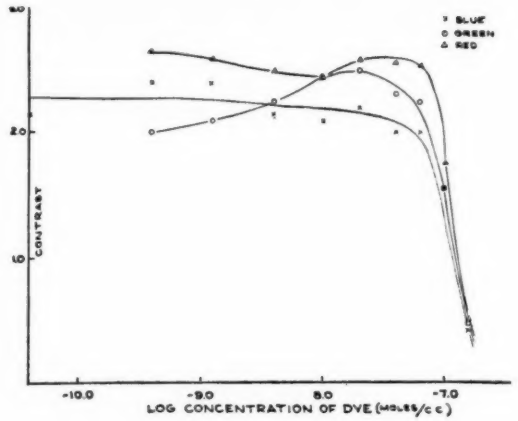

FIG. 2.

emulsion used. This concentration has been taken as a significant constant in the determination of the relationship between sensitizing and grain surface. The second significant figure is the total surface of the silver halide in the emulsion.

The surface area for each emulsion was determined from the projective area of the average grain, the number of grains per cubic centimeter, the silver content of the emulsion, and the density of the silver bromide. For the present purpose, since the experimental errors are fairly large, it is not critical how the projective area per cubic centimeter of emulsion is calculated. The total projective area has been obtained by multiplying the area of the average grain by the total number of grains, rather than by integrating the size frequency curve. The thickness of the average grain was calculated, assuming various projective shapes, e.g., an equilateral triangle, a circle, and a square. From these the thickness and total surface of a grain of each shape were calculated. It was found that with the assumption of different shapes, the surface area did not vary more than 15 percent, and the average of the three was taken as a measure of the total surface. An example of the calculations is as follows:

An emulsion was found by count to have 2.24×10^{10} grains per cubic centimeter. The projective area of the average grain was 8.6×10^{-9} cm^2. From the silver content and the density of silver bromide, the total volume of the average grain was calculated to be 25.4×10^{-14} cc, and the thickness 2.96×10^{-5} cm. For a square, the ratio of length of side to thickness is 3.1. For an equilateral triangle, the ratio of length of side to thickness is 4.8, and for a circle, the ratio of radius to thickness is 1.8. From these values, the total surface is found to be:

Triangle:	3.4	times	projective	area
Square:	3.3	"	"	"
Circle:	3.1	"	"	"

The average of these values, 3.3, was used to calculate the total surface of the emulsion.

In Table I are collected the results of the concentration studies.

It is seen immediately from the fifth column that the dye necessary for optimum sensitizing is directly proportional to the surface. The constancy of the ratio (dye/surface) for different emulsions is perhaps better than the size frequency data warrant, but since these were determined in a systematic manner by the same workers, errors should be uniform and reasonably constant. It is felt that, although the absolute values of the surface areas may be in error by as much as 50 percent, the relative values are much more accurate than this.

The emulsions used in this investigation were prepared, both from neutral silver nitrate and ammoniacal silver oxide solutions. These two types of emulsion were used, because it has been pointed out by Carroll and Hubbard[4] that the external habits of the silver bromide crystals are somewhat different in the two cases. The fact that these two types of emulsion show the

[4] B. H. Carroll and D. Hubbard, J. Phys. Chem. 31, 917 (1927).

same (dye/surface) ratio indicates that their surface characteristics are similar as regards sensitizing properties.

The constancy of the (dye/surface) ratio for emulsions of different types and of varying average grain size leads to the conclusion that the important factor in determining the concentration of dye necessary for optimum sensitizing is the degree of saturation of the surface of the halide with the dye. From these experiments it appears that the orientation or state of the adsorbed dye is the same with all of the emulsions studied, and hence that accidental irregularities in the crystals are not of major importance in determining concentration effects.

The question naturally arises as to what percentage of the sensitizer added to an emulsion is adsorbed to the silver halide. Experiments have shown that at least 99 percent of each of the sensitizing dyes used in the present experiments is adsorbed to the grain at the optimum sensitizing concentration. At concentrations of the dyes greater than optimal, the amounts of unadsorbed dye increase rapidly.

If it be arbitrarily assumed that the dye molecules lie flat on the surface of the halide, the data in Table I afford basis for estimation of the degree of surface saturation of the silver halide at the optimum sensitizing concentration. Dye II will serve as an example.

Dye II is an 8-alkylthiacarbocyanine. Estimates of the projective area of this molecule can be made by using the atomic radii values of Pauling and Huggins,[5] and assuming complete ionization of the halide. The estimate for dye II is 150A². Using this figure, together with the data of Table I, it is found that the projective area of the dye molecules adsorbed to one square centimeter of silver halide surface is nearly one square centimeter. This calculation is consistent with the view that at optimum sensitizing concentration, the surface of the silver halide grains in the emulsion is covered with a monolayer of dye molecules.

Sheppard and Crouch[1] and Sheppard, Lambert and Keenan[2] have calculated the numbers of surface bromide ions per dye molecule adsorbed at saturation for two cyanine dyes, Orthochrom T and Pinacyanol. The figure is 2.3 for Orthochrom T, and 1.7 for Pinacyanol. Bokinik[6] has reported a value of 10.0 for Pinacyanol. Similar calculations for the present experiments yield the figures: dye I, 10; dye II, 10; dye III, 20. The agreement with the result of Bokinik is good. The difference between the latter figures and those of Sheppard *et al.* may be explainable on the basis that saturation of the silver halide surface, as measured by effects on photographic sensitivity, is not the same as saturation obtained from a study of adsorption isotherms. This would be in confirmation of the results with Orthochrom T.[1] No direct comparisons can be made with the present data.

That the size of the dye molecule has a definite influence upon the concentration of dye at "sensitizing" saturation may be seen from the data of Table I. Dye II is a thiacarbocyanine, and dye III a thiadicarbocyanine. The number of moles of dye III which saturate the surface of the silver halide is about one-half that required of dye II. Since dye III is the larger molecule, this effect is in the right direction. In magnitude, however, the change in concentration is too large to be explained on a simple basis.

Evidence has been given[7] that cyanine dyes

TABLE I.

EMULSION	SURFACE cm^2/cm^3	DYE	OPTIMUM CONCENTRATION moles/cc emul. $\times 10^6$	Moles Dye / cm^2 surface $\times 10^{11}$
1	400	I	3.6	9.0
2	480		3.8	7.9
3	580		5.2	9.0
4	660		6.0	9.1
5	840		7.2	8.6
6	950		9.0	9.4
7	1080		12.0	11.1
1	400	II	4.4	11.0
3	580		6.3	10.9
4	660		8.0	12.1
6	950		11.2	11.8
7	1080		12.6	11.6
1	400	III	1.9	4.8
3	580		2.3	4.0
4	660		2.9	4.4
6	950		4.8	5.0
7	1080		4.8	4.4

[5] L. Pauling and M. Huggins, Zeits. f. Krist. **87**, 205 (1934).

[6] J. I. Bokinik, Kino-Photo Res. Inst. Moscow **3**, 14 (1935).

[7] J. A. Leermakers, B. H. Carroll and C. J. Staud, Communication No. 642 from the Kodak Research Laboratories this issue, p. 878.

adsorbed to silver halides are in an aggregated state. No strict definition of the term "aggregated" has been given, but, in general, the term is used to include those cases where two or more molecules interact with each other in such a way that the light absorption characteristics of the system are fundamentally different from those of the unassociated or simple dye molecule or ion. The sensitizing dyes used in this investigation have been found to be adsorbed in an aggregated state. Any statement concerning the orientation of the molecules at the surface of the halide must take cognizance of this phenomenon.

The fact that the calculations just described are in accord with the idea of a uniform, monomolecular layer of dye at the surface of the halide may result from coincidence. A second explanation is that the dye is adsorbed in multilayer patches, with a portion of the silver halide surface bare. A third possible structure of the system is that of a uniformly adsorbed layer, one molecule thick, with the dye molecules so oriented with respect to each other that definite interaction may take place, resulting in a shift of the absorption curve. The strict proportionality between concentration and surface is most easily explained on the basis of a uniform layer. To reconcile this with the evidence for aggregated adsorption is difficult, unless the structure is the third postulated above.

Acknowledgments

We wish to thank Mr. A. P. H. Trivelli and Mr. W. F. Smith for preparing several of the emulsions used in this work. The size frequency determinations were made by the Photomicrography Department of these Laboratories, under the direction of Mr. R. P. Loveland. We are also indebted to Mr. G. E. Fallesen for assistance with the sensitometric work.

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A Theory of Liquid Structure

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A simple model of the liquid is used to extend the equation of state previously obtained and to treat the process of fusion, viscous flow, and binary liquid systems. Our equation of state which applies to dense liquids has been fitted on to Happel's modification of van der Waals equation to give a single equation applicable over the entire range from gas to liquid. A liquid differs from a solid in that the surplus volume in one part of the liquid becomes available in another part without an activation energy appreciable as compared to kT. This communal sharing of volume gives rise to an entropy of fusion R modified, of course, if there are other structural changes. Other entropy changes arise from expansion, changes of librations into free rotations and from polymerization. Double molecules held together by van der Waals forces are considered quantitatively and used in the explanation of viscous flow and deviations of the equation of state at the critical point. An explicit expression is given for the osmotic pressure of a binary liquid mixture. "Holes" are used to complete the analogy between critical phenomena for a one component system and critical solution phenomena of binary liquids. In binary liquids the presence of a lower critical solution temperature above which two phases exist results from hydrogen (or analogous) bonds or bridges between unlike molecules which prevent free rotation. The critical mixing point coincides with the onset of free rotations which disrupt these bonds.

Introduction

In this paper, we extend the theory of liquids developed in previous papers.[1-3] By using a simple model it is possible to compute the physical properties and to examine in detail the processes of melting and of vaporization. In developing a theory for the structure of liquids it is sufficient to focus our attention on the free energy or on the partition function since all of the thermodynamical properties can be readily computed

[1] Henry Eyring, J. Chem. Phys. **4**, 283 (1936).
[2] Roy Newton and Henry Eyring, Trans. Faraday Soc. **33**, 73 (1936).
[3] H. Eyring and J. Hirschfelder, J. Phys. Chem. **41**, 249 (1937).

from either one.[4] We can express the Helmholtz free energy, A, in terms of the partition function for the liquid, f^N. Thus

$$A=-kT\log(f^N/N!)=E-TS. \quad (1)$$

Here N is Avogadro's number, E is the internal energy of the liquid, and S is its entropy. The Gibbs free energy, F, is therefore

$$F=H-TS=A+pV=pV-kT\log(f^N/N!), \quad (2)$$

where H is the heat content, p is the external pressure acting on the system, and V is the volume occupied by one mole of the liquid. From the thermodynamical relation, $S=-(\partial A/\partial T)_V$, and from (1) it follows that

$$S=R\log(f/N!)+RT(\partial\log f/\partial T)_V. \quad (3)$$

Similarly the internal energy, specific heats, etc. can all be expressed in terms of the partition function of the free energies. The equation of state for the liquid arises from the thermodynamical identity, $p=-(\partial A/\partial V)_T$, and Eq. (1). Thus:

$$p=-RT(\partial\log f/\partial V)_T. \quad (4)$$

The vapor pressure of the liquid is evaluated by equating the Gibbs free energy of the gas to that of the liquid as has been previously discussed.[3] In a similar way, the condition for the solid and the liquid phases to be in equilibrium at the melting point is for their respective Gibbs free energies to be equal. Since the free energy of crystals has been studied extensively, our conception of the melting process depends on the determination of the partition function or free energy of the liquid.

The partition function for a liquid, f^N, is the product of two factors: J^N and $B(T)$. Here J is the partition function for the internal electronic, vibrational, and rotational states of the molecules. The factor $B(T)$ is the partition function for the translational motions of the molecules. Thus:

$$f^N=J^NB(T),$$

where

$$B(T)=\int\cdots\int\exp(-W/kT)dx_1\cdots dz_N dp_{x1}\cdots dp_{zN}. \quad (5)$$

The integration is taken over the whole of phase space, and W is the energy of the system for a particular configuration in phase space. Even when W is known explicitly, we do not know how to evaluate $B(T)$. Joseph Mayer[5] and his coworkers are trying to evaluate $B(T)$ directly by making an expansion of the exponential, $\exp(-W/kT)$, into products of functions involving only two molecules. However, this approach is fraught with mathematical difficulties and we have attacked the problem in a different way. We define a "free volume," V_f, such that:

$$f^N\equiv[V_f(2\pi mkT/h^2)^{\frac{1}{2}}J]^N\exp(-E/kT). \quad (6)$$

Here m, k, h, and T are the mass of the molecules, Boltzmann's constant, Planck's constant, and the absolute temperature respectively. The whole burden of our ignorance is thus shifted to the free volume. However, the advantage of using Eq. (6) for the partition function is that V_f is simply the effective volume accessible to the center of a molecule in the liquid and is susceptible to a pictorial representation. Various models for the free volume are considered in this paper. The validity of these models is tested by comparing the calculated with the experimentally observed properties of the liquid.

Here as previously,[3] we assume that the total free volume in a liquid, as in a gas, is shared by all of the molecules. This distinguishes it sharply from the solid for which partition functions such as Einstein's and Debye's for high temperatures, treat each molecule as though it were restrained to the fraction of the total volume in the immediate neighborhood of the lattice point. A simple analogy makes the point clear. If one partitions a container into N equal compartments and puts one molecule into each, then by simply removing the partitions the entropy of the gas increases by R units provided that the partitions occupy a negligible volume and the molecules behave as a perfect gas.[6] If as the partitions are

[4] See for example, R. H. Fowler, *Statistical Mechanics*, second edition (Cambridge Press, 1936), particularly chapter VI. In this paper we use the G. N. Lewis notation for thermodynamical quantities whereas Fowler calls the Helmholtz free energy F and the Gibbs free energy G (see footnote page 530).

[5] J. Mayer, J. Chem. Phys. 5, 67 (1937); Mayer and Ackermann, J. Chem. Phys. 5, 74 (1937).

[6] This may be seen as follows. If the volume of the container is Nv, the partition function of the molecules when the partitions are absent (in analogy with the liquid) is

$$f^N=(Nv)^N(2\pi mkT/h^2)^{3N/2}. \quad (1)$$

Now when the partitions are present (corresponding to the

removed there is an expansion or if the compartments and molecules have such a shape that there is no free rotation then there will be additional entropy changes. These partitions which restrict the molecules to their aliquot portions of the total volume also prevent diffusion or viscous flow so that a theory of melting modeled along this line will automatically explain the enormous viscosity of solids as well as the entropy of melting. Now for actual solids the compartment walls are provided by the interlocking of the neighbors surrounding a particular molecule. As the system expands a point is reached when the neighbors no longer interlock and our partitions have just disappeared. At this point if a hole appears at anywhere in the system it can be transferred (made available) to any other point in the system without appreciable activation energy compared to kT. The system under such circumstances is a liquid. Thus a system on melting acquires a communal sharing of volume and with it a communal entropy R.

The Theory of Fusion

In a crystal, in contrast to a liquid there is a very high energy of activation for the process involving the movement of a molecule from one lattice point to an equivalent lattice point even if a hole is at the second. The high repulsive forces that act when a molecule approaches others as closely as it must in order to permit displacement give rise to this high activation energy for plastic flow in crystals. According to this argument one would expect that this heat of activation would decrease with temperature, the more rapidly the greater the coefficient of expansion of the crystal. Since in a simple cubic lattice a molecule need not approach closely to others in moving to an equivalent point, no crystals should exist with simple cubic structure, and none have been observed. Body-centered crystals of the NaCl type are of course different in that nearest identical atoms lie at the centers of neighboring cubes. This suggests that the criterion for the density of the liquid at the melting point is that a particle can just pass into a neighboring unoccupied point providing it has the energy kT in the corresponding degree of freedom. An ideal NaCl type lattice with two kinds A and B of incompressible uncharged spheres of equal radii should then melt to a body-centered liquid having a volume approximately 20 percent greater than that of the crystal at the absolute zero. For compressible molecules this figure will be somewhat lower. This is approximately the excess in volume of many liquids at the melting point over the volume of the crystal at the absolute zero.

With such a picture the process of melting becomes easy to understand. As the temperature rises a crystal expands until its volume is such that it is barely stable with respect to the more energy rich liquid. The liquid, in spite of its greater energy arising from its greater volume (unless there is a structural change in melting, as with water), is stable because of the communal use of the total free volume. Now the viscosity of a liquid rises as it is undercooled since the accompanying contraction throws it into that region where the lattice cannot collapse readily and therefore a molecule can no longer pass to a neighboring equivalent point without obtaining first the activation energy. Thus activation energy of flow increases as the volume decreases. We assume therefore that loss of fluidity parallels closely the loss of communal entropy. Both effects are related to the volume. Thus both are discontinuous upon fusion since the volume ordinarily changes abruptly during the course of crystallization. Changes in the communal entropy may be masked by larger changes due to loss of rotations, structural changes, etc.

If we think of a single crystal as a giant molecule then melting is simply a dissociation. Since the reverse association is a rate process with a large negative entropy of activation it may proceed excessively slowly in the absence of a suitable catalyst such as small crystals or dust

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solid) the partition function is

$$f'^N = N!v^N(2\pi mkT/h^2)^{3N/2} = (Nv/e)^N(2\pi mkT/h^2)^{3N/2}. \quad (2)$$

The $N!$ arises from the possibility of permuting the N molecules in the N compartments. Since the entropy for the system without partition is $S = k \ln (f^N/N!) = R \ln (fe/N)$ (using Sterling's approximation $N! = N^N e^{-N}$) and with partitions is $S' = k \ln (f/N)^N$, we see that $S - S' = R$. Therefore when we consider the molecules in the liquid as utilizing the available volume in a gas-like manner, we are using a picture essentially different from Guggenheim who considers the liquid as a quasi-solid with a partition function related to (2). Our partition function, related to (1), is therefore greater by e and our vapor pressure less by e per molecule than would be calculated on Guggenheim's model [see reference 4, chapter XIII].

particles. However, even if the stable crystal fails to appear a certain amount of molecular aggregation will accompany a fall in temperature. Thus a glass will consist of those aggregates in general having a different structure from the stable crystal and immersed in a matrix of randomly oriented molecules, depending on the temperature and the rate of cooling almost every volume and viscosity intermediate between liquid and crystal can in this way be realized.

In general melting is accompanied by an increase in the "free volume," V_f, although the total molal volume may increase or decrease depending on the structural changes. Thus although water contracts when it melts, the centers of mass of the individual water molecules have greater freedom of motion due to the breaking up of the quartz-like structure of ice.[7] This provides an explanation of certain increases in the entropy of melting over the communal value R. Dissociation of a mole of the crystal into double molecules yields a communal entropy of $\frac{1}{2}R$ only, giving a lower value than would otherwise be expected.

The entropy of fusion for monatomic crystals is made up of the communal entropy R plus small correction terms due to the expansion of the lattice during melting. These correction terms follow from the partition function. We will discuss various forms for the free volume in a later section of this paper. For monatomic liquids and particularly for the metals, the free volume of Kincaid and Eyring[8] gives very good results. They take

$$V_f = N\left[\left(\frac{h^2}{2\pi mkT}\right)^{\frac{1}{2}}\frac{T}{\theta_l}+2\left(\frac{V_l}{N}\right)^{\frac{1}{3}}-2\left(\frac{V_s}{N}\right)^{\frac{1}{3}}\right]^3. \quad (7)$$

The corresponding entropy of the liquid can be computed from (3) and (6). The partition function for a crystal is

$$\mathfrak{Z}(T) = (T/\theta_s)^3\, e^{-E'/kT} \quad (8)$$

and the corresponding entropy for the crystal is

$$S_s = R\log \mathfrak{Z}(T) + RT^2\,(d\log \mathfrak{Z}/dT) \quad (9)$$

performing the indicated operations, we obtain Eq. (11) of Kincaid and Eyring. Letting $\Delta S_f = \Delta S_t + \Delta S_j$ be the change of entropy on fusion:

$$\Delta S_t = -\tfrac{1}{2}R + 3R\ln\left[\frac{\Theta_s}{\Theta_l}+2\left(\frac{2\pi mk}{h^2T}\right)\frac{\Theta_s}{N^{\frac{1}{3}}}(V_l^{\frac{1}{3}}-V_s^{\frac{1}{3}})\right] \quad (10)$$

$$+3RT\left[\frac{1+\frac{4}{3}N^{-\frac{1}{3}}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{1}{2}}\Theta_l(\alpha_l V_l^{\frac{1}{3}}-\alpha_s V_s^{\frac{1}{3}})}{2T+4\left(\frac{2\pi mkT}{h^2}\right)^{\frac{1}{2}}\Theta_l N^{-\frac{1}{3}}(V_l^{\frac{1}{3}}-V_s^{\frac{1}{3}})}\right].$$

Here Θ_s, Θ_l, V_s, V_l are the characteristic temperatures and molal volumes of the solid and liquid respectively. ΔS_j is the entropy change associated with the degrees of freedom other than translation, i.e. with rotational and librational freedoms. The Debye characteristic temperature Θ_s is derived from the heat capacities of the solid at constant volume, $\alpha = (1/V)(\partial V/\partial T)_P$ is the coefficient of expansion. In the calculations which appear in Table I the term involving the coefficient of expansion is neglected. This is justifiable except perhaps in the case of argon. We have calculated ΔS_f first taking $\Theta_l = \Theta_s$ and then with $\Theta_l = 1.1\Theta_s$. The experimental S_f are from the tables of Kelley,[9] the molal volumes from Landolt-Börnstein. The values of Θ_s were taken from Eucken.[10]

The agreement between the last two columns is surprisingly good in view of our rough model. There are two reasons why one might expect a larger Θ for the liquid than for the solid. In the first place Θ for the solid rises regularly with temperature, and therefore with volume,[11] so that

TABLE I.

SUBSTANCE	T_f	Θ_s	V_l	V_s	ΔS_f*(calc)	ΔS_f†(calc)	ΔS_f(exp.)
A	84	85	28.0	25.1	3.24	2.78	3.32
Hg	234	84	14.7	14.2	2.89	2.42	2.38
Pb	600	88	19.5	18.8	2.63	2.12	2.17
Na	371	172	24.8	24.2	2.43	1.90	1.70
K	337	100	47.0	45.9	2.38	1.85	1.70
Cs	299	42	72.3	70.4	2.41	1.88	1.67
Cu	1356	315	8.00	7.60	2.91	2.43	2.36
Ag	1234	215	11.5	11.1	2.68	2.18	2.19
Au	1336	170	11.45	10.9	2.95	2.48	2.34

* $\Theta_l = \Theta_s$.
† $\Theta_l = 1.1\,\Theta_s$.

[7] Bernal and Fowler, J. Chem. Phys. **1**, 515 (1933).
[8] Kincaid and Eyring, J. Chem. Phys. **5**, 587 (1937).
[9] K. K. Kelley, Bull. 393, Bureau of Mines, 1936, pp. 134–138.
[10] Eucken, *Grundriss der phys. Chem.*, fourth edition (1934).
[11] Cf. Fowler, *Statistical Mechanics* (Cambridge Press, 1936), p. 131.

we might expect the same rise to continue in the expansion from solid to liquid. The real reason probably lies in the fact that in our model we have assumed the molecule is force free in the part of the "free volume" added by the expansion in melting and this requires a compensating change in the Θ. Kincaid and Eyring have found that a model in which the mercury atoms of the liquid, at the melting point, move with simple harmonic motion, accounts best for the specific heat results. In this case Θ is smaller for the liquid than for the solid.

The agreement, however, indicates that the point of view is not far wrong. As was mentioned above, if the crystal dissociates into diatomic molecules the communal entropy increase would be $\frac{1}{2}R$ instead of R E.U. The calculated entropies in column six differ from those in column eight of Table I by 0.5 to 0.7 E.U. This might be accounted for by partial polymerization, but the small decrease in conductivity indicates that polymerization is probably not important. On the other hand the small discrepancy which exists between the last two columns for the alkali metals may be due to association. Gordon's[12] calculations of the gas phase equilibria for the reactions $2M \rightleftharpoons M_2$ indicate a strong tendency for the alkalies to associate. The conductivities of the alkalies are not abnormally depressed upon fusion, which indicates that the gas phase equilibria cannot be more than suggestive for the condensed phase.

Mott and Jones[13] point out that the electronic contributions in metals to the heat capacity and therefore the entropy of melting is negligible.

Walden[14] and Kordes[15] have discussed entropies of fusion empirically. Walden came to the conclusion that $\Delta S_f = 13.5 \pm 1$ E.U. for most substances and he attributed values much lower to association. Kordes examined the entropies of fusion of the elements and found 2.2 E.U. to be the average value. It may be seen from our formulation that a value in the vicinity of 2–3 E.U. is to be expected for substances for which the partition function $J(T)$ is the same in the liquid and the crystal, i.e., if the rotational, vibrational and structural entropy changes may be neglected.

The most common changes in $J(T)$ are those associated with librations changing to free rotations.[16] Anomalous heat capacity regions and transitions in the solid were discussed from this point of view by Pauling.[16a] Examination of heat of fusion data and comparison with solid-solid transition data leads to the following criterion for free rotations in the solid; polyatomic molecules whose entropies of fusion are much lower than those of structurally similar molecules must have acquired at least one degree of rotational freedom before melting.

In Table II we have the data for a group of structurally similar compounds (Landolt-Börnstein), ΔS_f is the entropy of fusion at the temperature T_f°K, and T_t the temperature of observed solid transition.

Timmermans[17] gives 2.0 E.U. for the entropy of fusion of tertiary butyl chloride. According to our rule it should show a transition in the crystal. Smyth and Baker[18] in this laboratory have investigated the dielectric constant of this compound below its melting point. They find a transition at 219.3°K. From the relatively long constant temperature period they conclude that the transition has a large heat effect associated with it as would be expected from the small entropy of fusion.

From consideration of our partition function in connection with the data available in Landolt-Börnstein and Kelley's tables (reference 9) we have been led to the following conclusions with respect to entropies of fusion. Instead of the entropy of fusion of structurally similar molecules

TABLE II.

SUBSTANCE	T_f°K	ΔS_f	T_t°K	ΔS (TRANSITION)
Cyclopentane	179	1.06	121.6	9.6
Cyclohexane	279.7	2.32	186	8.6
Cyclohexanol	297	1.44	263.5	7.45
CH_3 cyclopentane	130.1	12.6	—	—
CH_3 cyclohexane	146.2	10.9	—	—

[12] Gordon, J. Chem. Phys. **4**, 100 (1936).
[13] Mott and Jones, *Properties of Metals and Alloys* (Oxford Press, 1936), pp. 178–81.
[14] Walden, Zeits. f. Electrochem. **14**, 713 (1908).
[15] Kordes, Zeits. f. anorg. allgem. Chemie **160**, 67 (1927).
[16] (a) Pauling, Phys. Rev. **36**, 430 (1930); (b) Fowler, Proc. Royal Soc. **149**, 1 (1935); (c) Fowler, ibid. **151**, 1 (1935).
[17] Landolt-Börnstein, Phys. Tafeln. Third Erganz. 3 (1936).
[18] Smyth and Baker, private communication.

being the same, the sum of entropies of transition and entropy of fusion of structurally similar molecules tends to be a constant. For diatomic molecules this sum is about 6 E.U. with deviations related to the moment of inertia of the molecule. For polyatomic molecules which can gain three degrees of rotational freedom the entropy of fusion is about 8.7 E.U. If a polyatomic molecule can gain more than three degrees of rotational freedom this sum is larger than 8.7 by an amount related to the number of extra rotations it can gain. The normal aliphatic hydrocarbons and normal alcohols are examples of the latter type.

The boiling point rules such as those in Hückel[19] are explained by considering the differences in rotational freedom in liquid and in gas. Thus of two otherwise similar molecules which are unable to rotate in the liquid about a particular axis, the one with the larger moment of inertia about that axis has the higher vapor pressure. This accounts very nicely for the rules referring to branched chain compounds and for the observed isotope effects with deuterium compounds. This is of interest here as it shows that some complicated molecules gain additional rotational freedom after melting.

As was mentioned above Pauling[16a] found that the changes in heat capacity which accompany transition in the solid can be accounted for in several simple substances by assigning a frequency of libration of 50 cm^{-1}. In Table III we have calculated $\Delta S_f = R + S_{rot} - S_{lib}$ which is to be compared with the observed ΔS_f. In calculating S_{rot} the necessary moments of inertia were taken from Sponer.[20] The frequency of libration was taken as 50 cm^{-1} in all cases. The experimental values are from Kelley (reference 9).

Thus our theory of a communal entropy of melting of R E.U. with additional entropy terms due to volume change and increased rotation usually leaves only small terms to be accounted for by structural changes and association.

TABLE III.

SUBSTANCE	T_f°K	S_{rot}	S_{vib}	ΔS_f(calc)	ΔS_f(exp.)
CL_2	238.4	13.60	8.75	6.84	6.77
Br_2	266	16.05	9.91	8.85	9.51
I_2	386.5	18.30	10.70	9.59	9.45
CS_2	161.1	14.50	7.20	9.29	8.37
N_2O	182.3	13.40	7.70	7.69	8.58

[19] Hückel, *Theor. Gr. der Org. Chem.* II, second edition (Leipzig, Akademische verlagegesellschaft, 1935), p. 122.
[20] Sponer, *Molekulenspecktren*, Vol. I (Springer, 1935).

EQUATION OF STATE

The virial theorem can be used to calculate the free volume or to determine the equation of state. For simplicity each molecule is considered as effectively moving in a cubical space which is proportional to v (the volume of the liquid divided by the number of molecules): If v_f is the free volume divided by Avogadro's number, $v_f^{\frac{1}{3}}$ is the mean distance which the center of the molecule moves in traveling between parallel faces. The average force acting on a molecule is the sum of the internal pressure, p_i, and the external pressure, p_{ex}, times the area of a face of the cube. Therefore the virial theorem of Clausius shows that the mean kinetic energy of molecules in a liquid is proportional to $(p_i+p_{ex})v^{\frac{1}{3}}v_f^{\frac{1}{3}}$. Since this mean kinetic energy is proportional to kT for most reasonable distributions of potential and kinetic energies, we have the equation

$$(p_i+p_{ex})v^{\frac{1}{3}}v_f^{\frac{1}{3}} = SkT. \tag{11}$$

Using the same model but proceeding somewhat differently, the proportionality factor, S, was found in an earlier paper[3] to be 2 for normal liquids. This value for S leads to satisfactory agreement between calculated and observed vapor pressures. S must decrease to unity for the gas. We now use the equation

$$v_f = S^3[v^{\frac{1}{3}} - d]^3. \tag{12}$$

This is Eq. (8) of an earlier paper[3] in a slightly changed notation. Combining Eqs. (11) and (12) we obtain

$$v_f = \left[\frac{SkT}{(p_i+p_{ex})(d+v_f^{\frac{1}{3}}/S)^2}\right]^3. \tag{13}$$

Here d is the collision diameter of the molecules times a constant depending on the type of packing of the molecules. This relation is important since it shows that *the free volume of a molecule at a particular temperature and pressure depends only on the internal pressure of the liquid in which it is immersed.* We shall have occasion to

use this form for the free volume when we consider binary solutions.

We can estimate the free volume for the liquid in another way. The free volume, v_f, is taken to be equal to the effective volume in which the center of a molecule can move when all of its neighbors are held fixed in their mean positions. This treatment is similar to that which Grüneisen used successfully for the case of solids.[21] The free volume is dependent on the type of packing in the liquid. If all of the forces acting on a molecule are balanced so that the molecules move in an essentially force free region until they collide at some effective separation d, the free volumes, v_f, may be obtained by the application of solid geometry. Thus for simple cubic packing the equation

$$v_f = 8(v^{\frac{1}{3}} - d)^3 \tag{14}$$

was obtained in an earlier paper.[3] Here $v = V/N$ where V is the molal volume of the liquid and N is Avogadro's number. In types of packing where the free volume is similar in shape to the unit cell of the lattice, it is possible to prove the general theorem that the free volume is:

$$v_f = 8(v^{\frac{1}{3}} - v_0^{\frac{1}{3}})^3, \tag{15}$$

where v_0 is defined as the volume of the liquid per molecule v when the molecules are crowded so close together that the nearest neighbors are separated by the diameter of the molecules d. In those types of packing where the free volume is truncated by the neighboring molecules and is no longer similar in shape to the unit cell the free volume must be computed as a special case. Thus we find that for body-centered cubical packing:

$$v_f = 9(v^{\frac{1}{3}} - (4)^{\frac{1}{3}}3^{-\frac{1}{2}}d)^3. \tag{16}$$

Since b, the usual van der Waals constant, is four times the actual volume occupied by the molecules, it is convenient to use $[(3/\pi)(b/2n)]^{\frac{1}{3}}$ for the collision diameter. Thus for body-centered packing we have

$$v_f = 9(v^{\frac{1}{3}} - 0.7163(b/N)^{\frac{1}{3}})^3, \tag{17}$$

which leads to the equation of state

$$(p + a/V^2)(V - 0.7163b^{\frac{1}{3}}V^{\frac{2}{3}}) = RT. \tag{18}$$

[21] E. Grüneisen, Ann. d. Physik **39**, 257 (1912).

Now in this equation of state (18) the term which acts like the "excluded volume" of the van der Waals equation is $0.7163V^{\frac{1}{3}}b^{\frac{2}{3}}$. van der Waals, Boltzmann, Jaeger and others realized a long time ago that the excluded volume was a function of volume and tried to make the necessary corrections to the equation of state for dense gases. Happel[22] using one of Boltzmann's methods made the most extensive corrections to the equation of state for the geometrical overlapping of hard spheres. Happel's equation of state has recently been rederived by Rameshchandra Majumdar.[23] This equation has the form:

$$\left(p + \frac{a}{V^2}\right) = \frac{RT}{V}\left[1 + \frac{b}{V} + \frac{5}{6}\left(\frac{b}{V}\right)^2 + 0.2869\left(\frac{b}{V}\right)^3 + \cdots\right]. \tag{19}$$

Since our Eq. (18) should hold for dense liquids and Happel's (19) should hold for moderately concentrated gases we piece them together by adding another term onto Happel's. Thus we obtain

$$\left(p + \frac{a}{V^2}\right) = \frac{RT}{V}\left[1 + \frac{b}{V} + \frac{5}{8}\left(\frac{b}{V}\right)^2 + 0.2869\left(\frac{b}{V}\right)^3 + 0.1928\left(\frac{b}{V}\right)^4\right]. \tag{20}$$

Eq. (20) agrees with (18) when V is small, i.e. around $V = \frac{1}{2}b$, and with (19) when V is large. The free volume corresponding to (20) is

$$V_f = V\exp\left\{-\left[\frac{b}{V} + 0.3125\left(\frac{b}{V}\right)^2 + 0.0956\left(\frac{b}{V}\right)^3 + 0.0482\left(\frac{b}{V}\right)^4\right]\right\}. \tag{21}$$

This free volume agrees with (17) for small volumes. Fig. 1 shows the good fits that were obtained.

Since our equation of state (20) involves only the van der Waals constants we can calculate

[22] H. Happel, Ann. d. Physik **4**, **21**, 242 (1906).
[23] R. Majumdar, Bull. Calcutta Math. Soc. **21**, 107 (1929).

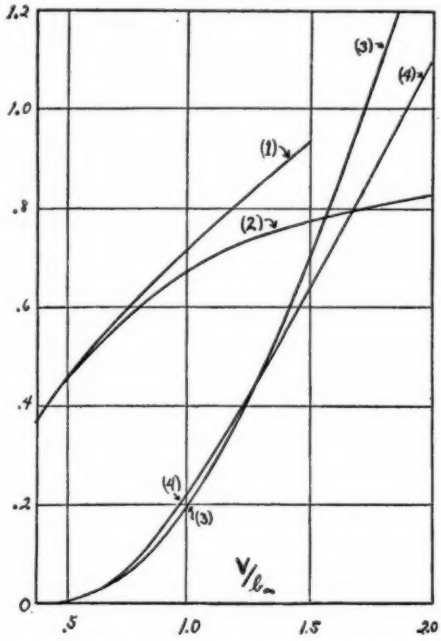

FIG. 1. Curves (1) and (2) are the excluded volumes, $b_v \equiv RT/(p+a/V^2)$, in units of b_∞ as computed from the equation of state for the dense liquid and from the modified Happel equation, respectively. Curves (3) and (4) are the free volumes, V_f, in units of b_∞ as computed from the partition function for the dense liquid and from the modified Happel partition function respectively. It will be noticed that curves (1) and (2) and also curves (3) and (4) lie close together throughout the range of liquid volumes.

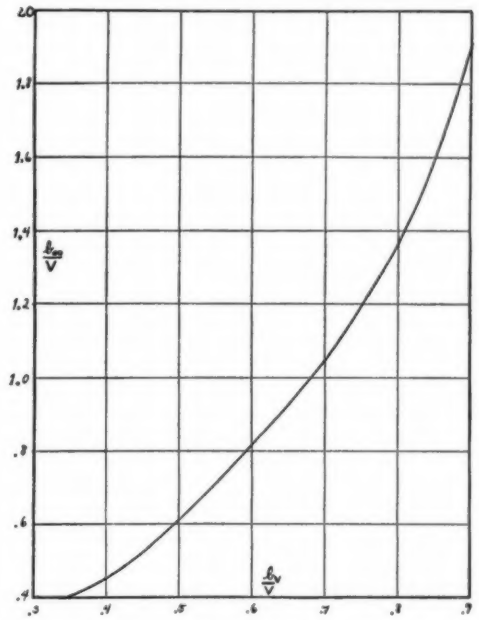

FIG. 2. Relationship between van der Waals constant, b_∞, and the experimental quantity, $b_v = V - RT/(p+a/V^2)$. This curve is useful in computing the value of b_∞ from the p, V, T for a liquid.

these from two values of p, V, T. Or given a, p, V, and T we can readily calculate b. Thus in Fig. 2, b/V is plotted against the experimental quantity $b/V = 1 - RT/(pV+a/V)$. The quantity b calculated in this manner from the simple van der Waals' equation using experimental values of p, V, and T is called the excluded volume. It is not a constant and only in the limit of large volumes becomes equal to van der Waals b. This latter quantity, as we have seen, is temperature dependent. Of course b should be independent of volume.

In Table IV, we have calculated the values of b from the experimental values of a and the p, V, T of the liquids both near the ordinary boiling point and at the critical point. In general the b's calculated for the normal liquid range are somewhat greater than those calculated at the critical point. The values of b calculated from the data in the normal liquid range agree well with the values which Wohl[24] finds are indicated by the behavior of the second virial coefficients, i.e. his b is approximately one and one-third times the value computed from van der Waals equation at the critical point. This disagreement with the van der Waals value is not serious since van der Waals equation is only adequate for gases much more dilute than those at the critical region. This inaccuracy of the van der Waals equation is illustrated by the disagreement between the experimental value of $p_c V_c/RT_c$ which is between 3.2 and 4.0 and the calculated value 2.6. A valid objection to our equation arises from the fact that it is only a little better than van der Waals in the critical region. This discrepancy is corrected later by taking account of clustering and the temperature dependence of b.

TEMPERATURE DEPENDENCE OF COLLISION DIAMETERS

Since molecules are not rigid both a and b vary with temperature. Lennard-Jones[25] has con-

[24] K. Wohl, Zeits. f. physik. Chemie, Bodenstein Festbond, 807 (1931).

[25] E. Lennard-Jones, Chapter X, R. H. Fowler (second edition 1936).

sidered the mutual potential energy of two molecules. He finds that the second virial coefficient can be explained by taking the mutual potential,

$$E(r)=-c/r^6+l/r^{12}. \tag{22}$$

The inverse twelfth power of the repulsive potential is arbitrary to some extent but is sufficiently accurate for present purposes. From this potential curve (Fig. 3), it follows that the collision diameter

$$d_T=\left[\frac{2l}{c}\frac{1}{1+(1+2lkT/c^2)^{\frac{1}{2}}}\right]^{1/6}. \tag{23}$$

Here d_T is defined as the distance of closest approach of two molecules having the average relative thermal energy $\frac{1}{2}kT$. Obviously, the b which we have used in our equation of state is related to d_T.

To a first approximation we can express c and l in terms of a and b.

$$c=ab/(\tfrac{2}{3}\pi)^2N^3, \quad l=ab^3/(\tfrac{2}{3}\pi)^4N^5, \tag{24}$$

so that

$$d_T^3=\frac{b}{\frac{2}{3}\pi N}\left(\frac{2}{1+(1+2bRT/a)^{\frac{1}{2}}}\right)^{\frac{1}{2}}$$

$$=d^3\left(\frac{2}{1+(1+0.8\,T/T_c)^{\frac{1}{2}}}\right)^{\frac{1}{2}}. \tag{25}$$

An equation of state improved to take account of the temperature dependence should use d_T in place of the hard diameter d. This variation of d_T with temperature makes b at the critical point around five percent smaller than near the boiling point. This removes some of the discrepancy between the b's in Table I calculated at the critical and at the lower temperatures.

Kincaid and Eyring[8] have used for their temperature dependent diameter:

$$d_T=v_s^{\frac{1}{3}}-\frac{1}{2\theta}\left(\frac{Th^2}{2\pi mk}\right)^{\frac{1}{2}}. \tag{26}$$

Using the Lindemann rule for the characteristic temperature $\Theta=119(T_m/MV_S^{\frac{2}{3}})^{\frac{1}{2}}$ their expression reduces to

$$d_T=(V_s/N)^{\frac{1}{3}}[1-0.0618(T/T_m)^{\frac{1}{2}}]. \tag{27}$$

which has essentially the same temperature dependence as (25). It is possible to derive a relationship for Θ like that of the Lindemann rule by equating d_T of (25) with that of (26). Making the somewhat arbitrary identification of $(V_s/N)^{\frac{1}{3}}=d_0$ we get

$$\theta=\frac{7.35}{1-(2/\{1+(1+0.8T/T_c)^{\frac{1}{2}}\})^{\frac{1}{2}}}\left(\frac{T}{MV_s^{\frac{2}{3}}}\right)^{\frac{1}{2}}, \tag{28}$$

which is identical with the Lindemann relationship if $T=0.77T_c$.

By using a slightly different form for the mutual potential energy between a pair of molecules, closer agreement with Lindemann's constant could be obtained. Thus the present theory connects the collision frequencies of the corresponding solid.

TABLE IV.

	a	Liquid Near Normal Boiling Point		Critical Point	
	atm/cc² mole	b_0/V	b	b_0/V	b
A	1.27×10^6	0.839	44.3	0.396	35.7
CO_2	3.61	.789	53.3	.442	52.1
N_2	1.45	.850	55.9	.458	51.4
O_2	1.49	.861	46.8	.466	41.5
He	.035	.857	44.4	.421	29 5
Ne	.207	.819	24.4	.396	19.8
Kr	2.04	.812	55.1	.308	36.4
H_2	.352	.914	55 5	.408	32.1
Cl_2	6.32	.859	75.8	.434	66.2
CO	1.34	.842	55.4	.390	41.9
HCl	3.66	.872	53.1	.460	50.0
CH_4	2.28	.850	62.1	.432	52.5
Hg	8.10	.955			
H_2O	5.47	.920	39.7	.600	37.0

Double Molecules

Another cause for the breaking down of van der Waals type of equation of state, in the vicinity of the critical volume, is that the gas or liquid is really made up of a mixture of single, double, triple, etc. molecules. At larger volumes these polymerized species are rare because of their smaller total translational entropy and at smaller volumes they become less important also because of their small entropy arising from their inability to rotate freely. A mixture of single and double molecules should be an example of different sizes which Hildebrand[26] has examined

[26] J. Hildebrand, J. Am. Chem. Soc. 59, 794 (1937).

in detail. The partition functions, free energy, and equaton of state which is developed for ideal solutions in a later section of this paper is applicable to this case.

Fowler[27] has considered imperfect gases as a mixture of single and double molecules. Our treatment is an extension to dense gases and extended liquids. We define a double molecule in such a way as to include only those in which the two singles do not have sufficient relative kinetic energy to separate, i.e. they are chemically associated. The formal statistical mechanics for such a problem is developed by Fowler and by an obvious generalization of his Eq. (861) we obtain

$$n_1^2/n_2(n_1+n_2)=v_{f1}^2/v_{f2}g. \tag{29}$$

Here $$g=2^{\frac{1}{2}}(h^2/2\pi m_1 kT)^3 f_{\text{vib-rot}}, \tag{30}$$

where $f_{\text{vib-rot}}$ is the partition function for vibration and rotation for the double molecule. n_1 and n_2 are the number of single and double molecules in the system at equilibrium. v_{f_1} and v_{f_2} are the free volumes for the two species. The problem is therefore resolved into the computation of $f_{\text{vib-rot}}$ from the quantized vibrational and rotational states of the double molecule and a determination of v_{f_1} and v_{f_2} from the theory of ideal solutions.

From the mutual potential energy (22) for a pair of molecules it follows that the minimum energy is

$$E_{\min}=-D=-\frac{c}{4l}\approx\frac{-1}{4}\frac{a}{b}. \tag{31}$$

$E(r)$ can be fitted to a Morse curve having the same dissociation energy, the same curvature at the minimum, and the same separation at the minimum. This curve is:

$$E(r)=\frac{a}{4b}\left[\exp\left(-12\left(\frac{e}{r_{\min}}-1\right)\right)-2\exp\left(-6\left(\frac{r}{r_{\min}}-1\right)\right)\right], \tag{32}$$

where $r_{\min}=(2l/c)^{1/6}$. The vibrations and rotations of the double molecules are then treated like these quantities for ordinary diatomic molecules. The quantized vibrational and rotational energy levels are easily found by reference to any standard text on quantum mechanics. The number of quantized vibrational levels is equal to the first integer less than $(K+1)/2$ where $K=4\pi r_{\min}(2\mu D)^{\frac{1}{2}}/6h$ and $\mu=m_1m_2/(m_1+m_2)$. Thus we find that double molecules of A have 7 vibrational levels, CO_2-12, N_2-6, O_2-7, He-0, Ne-2, Kr-13, H_2-1, Cl_2-20, CO-6, HCl-11, CH_4-6, Hg-48, H_2O-11. A satisfactory approximation to the energy for the vth vibrational and jth rotational level is:

$$E_{v,j}=-D+(2D/K)(v+1)+j(j+1)h^2/8\pi^2 I. \tag{33}$$

Knowing the energy levels we can compute the vibrational-rotational partition function:

$$f_{\text{vib-rot}}=\frac{\omega}{4\pi}\cdot\frac{1}{2}\cdot\sum_{v,j}(2j+1)\exp\left[-\frac{E_{v,j}}{kT}\right]. \tag{34}$$

Here $\frac{1}{2}$ is the symmetry factor. ω is the average solid angle through which the molecule may rotate. The summation over j may be replaced

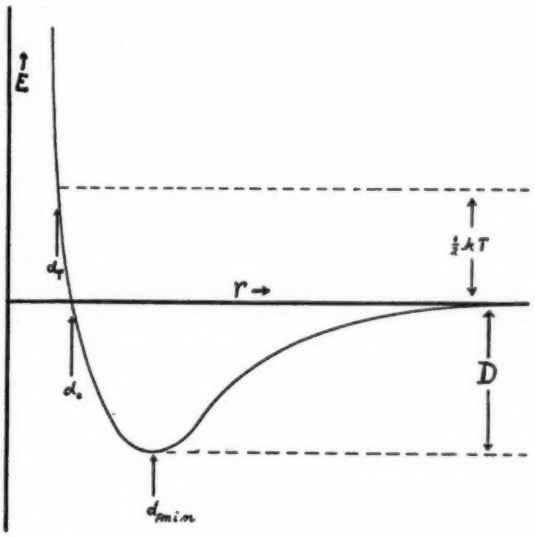

FIG. 3. Energy of interaction of two molecules, E, as a function of their separation, r. D is minus $E_{\min}$. The separations d_T, d_0, and $d_{\min}$ correspond to the potential energies of mutual interaction $\frac{1}{2}kT$, 0, and $E_{\min}$, respectively.

[27] R. H. Fowler, *Statistical Mechanics*, second edition (1936), p. 284.

by an integration

$$\sum_j (2j+1)\exp\left[-j(j+1)\frac{h^2}{8\pi^2 IkT}\right]$$
$$=\int_0^{j_{\max}}(2j+1)\exp\left[-j(j+1)\frac{h^2}{8\pi^2 IkT}\right]dj$$
$$=\frac{8\pi^2 IkT}{h^2}\left[1-\exp\left[-\frac{D}{kT}\left\{1-\frac{2}{K}(v+1)\right\}\right]\right]. \quad (35)$$

From which it follows that

$$f_{\text{vib-rot}}=\frac{\omega}{4\pi}\frac{8\pi^2 IkT}{2h^2}\left[-\frac{K+1}{2}+\exp\left(\frac{D}{kT}\left(1-\frac{2}{K}\right)\right)\frac{1-e^{-D/kT}}{1-e^{-2D/KkT}}\right]. \quad (36)$$

Using (36), the value of g is computed for a number of cases. For example g for argon is equal to 52.5 cc/N.

Next we must examine the free volumes for the single and for the double molecules. Clearly van der Waals association to double molecules cannot appreciably change the internal pressure. From Hildebrand's work on the paraffins it appears that the internal pressure for the pure components of an ideal solution are equal. Since the free volume can be written in the form

$$v_f=\left(\frac{SRT}{p_i+p_{ex}}\right)^3\frac{1}{(d+v_f/S^{\frac{1}{3}})^6}, \quad (13)$$

where d is nearly the hard diameter of the molecule. S is a constant very nearly equal to 2. To a first approximation $v_f^{\frac{1}{3}}$ is negligible compared with d and therefore

$$v_{f2}/v_{f1}=d_1^6/d_2^6. \quad (37)$$

From the work of Keesom,[28] on ellipsoidal molecules, it is easy to show that $4d_1^3>d_2^3>2d_1^3$. It would be difficult to obtain d_2 more accurately and so we shall take $d_2^3=3d_1^3$ as representing a mean between the two limiting values. Thus $v_{f_2}/v_{f_1}=1/9$. Because of the uncertainty in v_{f_2}/v_{f_1} it is not necessary to compute v_{f_1} with great accuracy.

[28] Keesom, Akad. van Wettenschappen te Amsterdam, Proc. Sec. Sci. **15**, 240 (1912).

$$v_{f1}=v\exp\left[-\left\{\frac{b_1}{V_1}+0.3125\frac{b_1^2}{V_1^2}+0.0956\frac{b_1^3}{V_1^3}+0.0482\frac{b_1^4}{V_1^4}\right\}\right]. \quad (38)$$

Here V_1 is the volume of the pure component one but for the accuracy demanded it is sufficient to use V, the volume of the mixture, in place of V_1. Thus for argon we find at the critical point $v_{f_1}=39$ cc/N

$$n_1^2/n_2(n_1+n_2)=6.7 \quad (39)$$

and therefore $n_2=0.13n_1$. If we had taken $d_2^3=4d_1^3$, $n_2=0.08$ and if $d_2^3=2d_1^3$, $n_2=0.26$. Thus there is a considerable proportion of the molecules near the critical point which are clustered into small chemically associated aggregates.

Next, we seek the equation of state for the gaseous argon mixture. Taking $b_2=3b_1$, $b_{12}=[(1+3^{\frac{1}{3}})/2]^3=1.82$,

$$b=\frac{n_1^2+3.64n_1n_2+3n_2^2}{(n_1+n_2)(n_1+2n_2)}b_1=1.070b_1. \quad (40)$$

Using this value of b in the equation of state, together with $V=75.2$ cc, $b_1=44.3$ cc,

$$p+\frac{a}{V^2}=\left(\frac{n_1+n_2}{n_1+2n_2}\right)\frac{RT}{V}\left[1+\frac{b}{V}+0.625\frac{b^2}{V^2}+0.2869\frac{b^3}{V^3}+0.1928\frac{b^4}{V^4}\right] \quad (41)$$

it follows that for argon at the critical volume

$$p+\frac{a}{V^2}=\frac{RT}{V-32.8}=\frac{RT}{V-b_v}. \quad (42)$$

Experimentally b_v is found equal to 29.8 cc so that our calculated "excluded volume," 32.8 cc, is in excellent agreement with experiment for the critical point when we take clustering of molecules into consideration. If we had corrected b_1 for temperature variation, the agreement would have been even better.

In making these calculations for the number of double molecules, it is tacitly assumed that the internal rotations of the individual molecules

remain unchanged. This is really true for gases of monatomic molecules such as A, Ne, Kr, etc. and for these molecules the equation of state is satisfactorily corrected by the consideration of double molecules. However, for nonsymmetrical molecules such as CO_2, H_2O, HCl the rotations of the single molecules are hindered by the formation of the double molecules. In these cases, the resulting loss in entropy due to the conversion of rotational into librational degrees of freedom renders the double molecules improbable. It will be noticed that in Table IV the agreement between b calculated from the normal liquid data are satisfactory for these cases without change. From this table it may be seen that methane is an example of a symmetrical polyatomic molecule in which these double molecules appear. Cl_2 and CO polymerizes, but O_2, N_2, and HCl show this tendency to a smaller extent.

Viscosity

We now propose a model for viscous flow. Any kinetic process proceeds by the fastest mechanism to the more or less complete exclusion of others. For a rate process to be rapid it must have a low free energy of activation which means a low energy of activation unless the decrease in entropy for activation is abnormally small. With these general considerations as a guide, the problem is to decide how one layer of molecules can slip by a neighboring layer with a minimum of activation energy for each individual process. The instantaneous formation of a double molecule, one from each layer, with an accompanying rotation through an arc of somewhat less than 90, depending on the packing, provides the most reasonable mechanism. This may be more clearly seen by reference to Fig. 4. The initial position of the molecules is represented by the dotted lines and after rotation they occupy the position indicated by the heavy black circles. The activation energy consists largely in the provision of the space, or the hole, to permit rotation. The experimental activation energy for viscous flow is in the neighborhood of a third to a fourth the heat of vaporization for many normal liquids so that we assume the required hole is about one-third to a fourth the space occupied by a molecule, since it requires the same energy

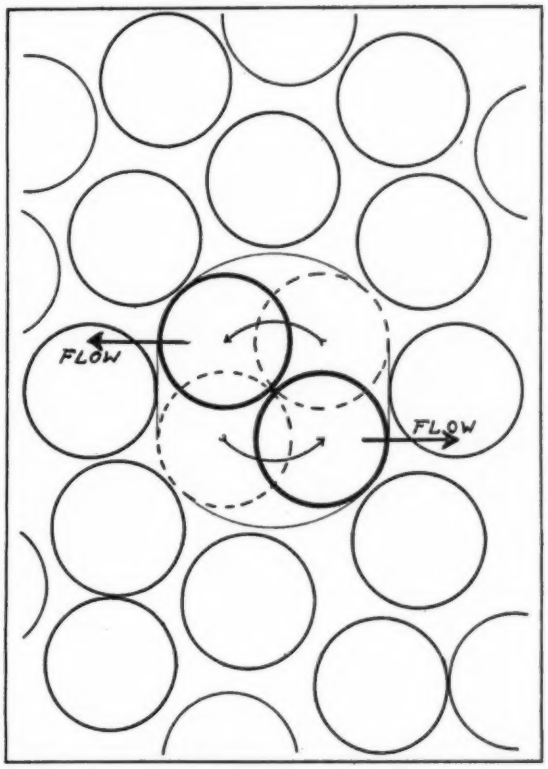

Fig. 4. Viscous flow by means of the rotation of double molecules. Two molecules collide to instantaneously form a double molecule. If there is sufficient space available, this double molecule can rotate and then dissociate. One layer of liquid can flow past another layer by a succession of these processes.

to make a hole of molecular size as to vaporize a molecule. When one takes account of the fact that the double molecule AB is compressed along its axis a simple geometrical calculation of the hole size required to permit this rotation leads to a value in satisfactory agreement with the experimental one. A careful examination of the available material by Ewell and one of the present authors shows that this general point of view leads to an adequate quantitative treatment of viscosity for a great variety of liquids over the entire pressure and temperature range.

Binary solutions

The equation of state and partition function for a binary solution can be formulated in much the same manner as for the pure liquids. We assume that the equation of state for a mole of the mixed liquid can still be written in the form:

$$(p+a/V^2)(V-0.7163\,V^{\frac{1}{3}}b^{\frac{1}{3}})=RT, \qquad (43)$$

where a and b are now functions of the mole fraction of the constituents. Hildebrand[29] and others have brought forth arguments in favor of using the following form for a:

$$a=a_1[1+N_2\alpha_1+N_2^2\alpha_2] \equiv N_1^2a_1+2N_1N_2a_{12}+N_2^2a_2, \quad (44)$$

where N_2 in the mole fraction of component two and a_1, a_{12}, a_2, α_1, and α_2 are constants independent of mole fraction. This form is strictly true if either N_2 is small or the pairs of like and unlike neighboring molecules are distributed at random. Guggenheim[30] develops a more complicated formula for a in order to correct for the nonrandomness of the distribution. However, Hildebrand points out that Guggenheim's correction terms are small for most actual cases and therefore we use the simpler formula (44). Fowler[31] and others have shown that b for a gaseous mixture should have the same form:

$$b=b_1[1+N_2\beta_1+N_2^2\beta_2] \equiv N_1^2b_1+2N_1N_2b_{12}+N_2^2b_2, \quad (45)$$

where b_1, b_{12}, b_2, β_1, β_2 are all constants independent of the mole fraction.

For a given pressure and temperature, the molal volume, V, is determined from Eq. (43) by the values of a and b. This molal volume is a function of the mole fraction of the constituents. From the equations

$$V=N_1\bar{V}_1+N_2\bar{V}_2$$

and $$\partial V/\partial N_2=\bar{V}_2-\bar{V}_1,$$

so that $$\bar{V}_1=V-N_2\partial V/\partial N_2, \quad (46)$$

and using Eq. (51) below we have the simple expression

$$\bar{V}_1=V\left\{1-\frac{N_2}{a/VRT-4}\left[\left(\frac{a}{VRT}-1\right)\frac{\partial \log b}{\partial N_2} -\frac{3\,\partial \log a}{\partial N_2}\right]\right\}. \quad (47)$$

Interchanging subscripts 1 and 2 gives $\bar{V}_2$. It is easy to show that

$$\left(\frac{\partial V}{\partial N_2}\right)_{T,\,p}=-\left(\frac{\partial p}{\partial N_2}\right)_{T,\,V}\Big/\left(\frac{\partial p}{\partial V}\right)_{T,\,N_2} \quad (48)$$

And from the form of (43), it follows that

$$\left(\frac{\partial p}{\partial N_2}\right)_{T,\,V}=-\frac{1}{V^2}\frac{\partial a}{\partial N_2} -\frac{1}{b}\frac{\partial b}{\partial N_2}\left[V\left(\frac{\partial p}{\partial V}\right)_T+p-\frac{a}{V^2}\right], \quad (49)$$

$$\left(\frac{\partial p}{\partial V}\right)_{T,\,N_2}=\frac{1}{3V^2}\left[4\frac{a}{V}-2pV-\frac{V^2(p+a/V^2)^2}{RT}\right]. \quad (50)$$

Neglecting p in comparison with a/V^2,

$$\left(\frac{\partial V}{\partial N_2}\right)_{T,\,p}=\frac{V}{a/VRT-4}\left[\left(\frac{a}{VRT}-1\right)\frac{\partial \log b}{\partial N_2} -3\frac{\partial \log a}{\partial N_2}\right]. \quad (51)$$

Taking the derivative of $\partial V/\partial N_2$ with respect to N_2:

$$\left(\frac{\partial^2 V}{\partial N_2^2}\right)_{T,\,p}=\frac{1}{V}\left(\frac{\partial V}{\partial N_2}\right)^2+\frac{1}{1-4VRT/a} \times\left[-\left(\frac{\partial V}{\partial N_2}\right)+V\frac{\partial \log b}{\partial N_2}\right]\left[-\frac{1}{V}\left(\frac{\partial V}{\partial N_2}\right)+\frac{\partial \log a}{\partial N_2}\right] +\frac{V}{a/VRT-4}\left[\left(\frac{a}{VRT}-1\right)\frac{\partial^2 \log b}{\partial N_2^2} -3\frac{\partial^2 \log a}{\partial N_2^2}\right]. \quad (52)$$

Eqs. (51) and (52) should be valid for any form of a and b and any value for the mole fraction.

The expansions of the volume about $N_2=0$ is of particular importance in studying the deviations from the laws for ideal solutions. Substituting the forms (44) and (45) for a and b into (51) and (52):

$$\frac{1}{V}\left(\frac{\partial N}{\partial N_2}\right)_{N_2=0}=\frac{\alpha_1(1-3x)-x\beta_1}{1-4x}\equiv\gamma_1, \quad (53)$$

[29] J. Hildebrand, Chem. Rev. **18**, 315 (1936).
[30] Guggenheim, Fowler's *Statistical Mechanics*, second edition (1936), p. 533.
[31] Fowler, *Statistical Mechanics*, second edition (1936), p. 250.

$$\frac{1}{V}\left(\frac{\partial^2 V}{\partial N_2^2}\right)_{N_2=0}=\frac{2}{1-4x}\Big[\alpha_2(1-3x)-\beta_2 x+(1/3)\beta_1^2 x-\alpha_1\beta_1 x+\gamma_1\{-\alpha_1(1-4x)+(4/3)x\beta_1+\gamma_1^2(1-14x/3)\}\Big].$$

Here x is defined as $x\equiv(1/3)(1-V_1RT/a_1)$. At the absolute zero temperature

$$\frac{1}{V}\frac{\partial V}{\partial N_2}=\beta_1,\quad \frac{1}{V}\frac{\partial^2 V}{\partial N_2^2}=2\beta_2,$$

which means that the volume of the mixture would be a function only of the sizes of the molecules and would not depend on the forces which bind them together. When $a_1/V_1RT=10$, which corresponds to the boiling point for substances which obey Trouton's rule, $(\partial V/\partial N_2)_{N_2=0}$ and $(1/V)(\partial^2 V/\partial N_2^2)_{N_2=0}$ have the particularly simple forms:

$$\frac{1}{V}\left(\frac{\partial V}{\partial N_2}\right)_{N_2=0}=(3/2)\beta_1-(1/2)\alpha_1, \tag{54}$$

$$\frac{1}{V}\left(\frac{\partial^2 V}{\partial N_2^2}\right)_{N_2=0}=3\beta_2-\alpha_2+2(\beta_1-\alpha_1)^2.$$

The partition function for the binary solution is formulated in much the same form as for the pure liquid.

$$f_l^{n_1+n_2}=\frac{(n_1+n_2)!}{n_1!n_2!}[(n_1+n_2)v_f]^{n_1+n_2}J_1^{n_1}J_2^{n_2}\times\left(\frac{2\pi m_1 kT}{h^2}\right)^{3n_1/2}\left(\frac{2\pi m_2 kT}{h^2}\right)^{3n_2/2}\cdot\exp(-E/kT), \tag{55}$$

where

$$v_f=\frac{V}{N}\exp-\left\{\frac{b}{V}+0.3125\frac{b^2}{V^2}+0.0956\frac{b^3}{V^3}+0.0482\frac{b^4}{V^4}\right\} \tag{54}$$

as in Eq. (50). J_1 and J_2 are the partition functions for the degrees of freedom of 1 and 2 other than translation. The factor $(n_2+n_2)!/(n_1!n_2!)$ is the number of physically different permutations of the two species. This term gives rise to an entropy of mixing.

The derivation of the free volume of molecules in the liquid by means of the virial theorem, holds as true for the case of binary solutions as for pure components. The size of the free volume for a molecule of species one depends only on the internal pressure which the neighboring molecules exert on it and on no other property of these molecules. Thus in the case of one hydrocarbon immersed in another, the free volumes of the molecules should be the same in the mixture as in the pure components since Hildebrand[25] finds that the internal pressure for this case is independent of mole fraction. The free volume, v_f, for a mixture of n_1 and n_2 molecules of species one and two is given by the relationship:

$$v_f^{(n_1+n_2)}=v_{f1}^{n_1}v_{f2}^{n_2}. \tag{54}$$

Here
$$v_{f1}=\frac{(SkT)^3}{(p'_1+p_{ex})^3(d+v_{f1}^{\frac{1}{3}}/s)^6}. \tag{55}$$

But v_{f1}/s is small compared to d and so we do not make any appreciable error in replacing v_{f1} in the term $d+v_{f1}^{\frac{1}{3}}/s$ by $(v_{f1}^0)^{\frac{1}{3}}$, the free volume of the pure component. Therefore

$$v_{f1}=v_{f1}^0(p_{i1}^0+p_{ex})^3/(p_{i1}+p_{ex})^3. \tag{56}$$

The resulting v_{f1} of (56) can now be substituted back into the denominator of (55) to obtain a still better value if desired. p_{i1} in (56) is the internal pressure acting on a molecule of species 1 in the solution and p_{i1}^0 is the internal pressure of the pure component. Usually p_{ex} is negligible compared to p_{i1}. Thus

$$f^{n_1+n_2}=V_{f1}^{0n_1}V_{f2}^{0n_2}p^{0}{}_{i1}^{3n_1}p^{0}{}_{i2}^{3n_2}/p_i^{3(n_1+n_2)}. \tag{57}$$

Here we introduce a mean internal pressure p_i which satisfies the relationship:

$$(n_1+n_2)\log p_i=n_1\log p_{i1}+n_2\log p_{i2}. \tag{58}$$

Eq. (43) for the mixed liquid when solved for the free volume leads to the identification $p_i=a/V^2$. Eq. (57) shows that the condition for the additivity of entropies of solutions is that p_{i1} and p_{i2} be independent of mole fraction.

Ideal solutions satisfy the two criteria—additivity of energy and of entropy. These conditions may be stated in terms of van der Waals a and the volume of the liquid. For

energy to be additive:

$$a/V=N_1a_1/V_1^0+N_2a_2/V_2^0. \tag{59}$$

For entropy to be additive, it follows from (19) that:

$$a/V^2=(a_1/V_1^{0^2})^{N_1}(a_2/V_2^{0^2})^{N_2}. \tag{60}$$

Solving (59) and (60) for a and for V

$$a=\left(\frac{V_1^{0^2}}{a_1}\right)^{N_1}\left(\frac{V_2^{0^2}}{a_2}\right)^{N_2}\left[N_1^2\frac{a_1^2}{V_1^{0^2}}+2N_1N_2\frac{a_1}{V_1^0}\frac{a_2}{V_2^0}+N_2^2\frac{a_2^2}{V_2^{0^2}}\right], \tag{61}$$

$$V=\left(\frac{V_1^{0^2}}{a_1}\right)^{N_1}\left(\frac{V_2^{0^2}}{a_2}\right)^{N_2}\left[N_1\frac{a_1}{V_1^0}+N_2\frac{a_2}{V_2^0}\right].$$

Eq. (61) for an ideal liquid shows that the volume is not the sum of the volumes of the components unless the internal pressures of the components are equal. If these internal pressures are equal for an ideal solution, it follows from (22) that $a_{12}=(a_1a_2)^{\frac{1}{2}}$.

The Gibbs free energy for a binary liquid, F_l, may be obtained from the corresponding partition function by means of the relation:

$$F_l=p_{ex}V_l-kT\log f_l^{n_1+n_2}/(n_1+n_2)!. \tag{62}$$

Using Eq. (51) for $f_l^{n_1+n_2}$:

$$F_l=p_{ex}V_l-kT\left[\frac{-E}{kT}+(n_1+n_2)(1+\log v_f)+n_1\log\left\{\frac{(n_1+n_2)}{n_1}J_{1l}\left(\frac{2\pi m_1kT}{h^2}\right)^{\frac{3}{2}}\right\}+n_2\log\left\{\frac{n_1+n_2}{n_2}\cdot J_{2l}\left(\frac{2\pi m_2kT}{h^2}\right)^{\frac{3}{2}}\right\}\right]. \tag{63}$$

Here V_f may be defined in a number of equivalent, but seemingly different, forms such as (52) and (57). From the free energy all of the thermodynamical properties of the binary solution are completely determined. A few of these properties will be discussed in detail.

The partial pressures[32] are determined in the usual way by the condition that at the equilibrium between liquid and vapor:

$$\begin{aligned}(\partial F_g/\partial n_1')_{T,\,V_g,\,n_2'}&=(\partial F_l/\partial n_1)_{T,\,V_g,\,n_2},\\ (\partial F_g/\partial n_2')_{T,\,V_g,\,n_1'}&=(\partial F_l/\partial n_2)_{T,\,V_g,\,n_1}.\end{aligned} \tag{64}$$

Here F_g is the free energy of the gas containing n_1' and n_2' molecules of species one and two respectively. The free energy for the molecules in the vapor is:

$$F_g=p_{ex}V_g-kT\left[(n_1'+n_2')\left[1+\log\frac{V_g}{(n_1'+n_2')}\right]+n_1'\log\left\{\left(\frac{n_1'+n_2'}{n_1'}\right)J_{1g}\left(\frac{2\pi m_1kT}{h^2}\right)^{\frac{3}{2}}\right\}+n_2'\log\left\{\left(\frac{n_1'+n_2'}{n_2'}\right)J_{2g}\left(\frac{2\pi m_2kT}{h^2}\right)^{\frac{3}{2}}\right\}\right]. \tag{65}$$

From (63):

$$\frac{\partial F_l}{\partial n_1}=-kT\left[\frac{1}{kT}\left[-\left(\frac{\partial E}{\partial n_1}\right)+kT\right]+\log\left\{\left(\frac{n_1+n_2}{n_1}\right)\left(\frac{2\pi m_1kT}{h_2}\right)^{\frac{3}{2}}\right\}+\log V_f+\left(\frac{n_1+n_2}{V_f}\right)\frac{\partial V_f}{\partial n_1}\right]+p_{ex}(\partial V_l/\partial n_1). \tag{66}$$

Considering the partial pressure of component one, p_1 is:

$$p_1=\frac{n_1'kT}{V_g}=\left(\frac{n_1}{n_1+n_2}\right)kTJ_{1g}\exp\left[-\frac{(n_1+n_2)}{V_f}\frac{\partial V_f}{\partial n_1}+\frac{1}{kT}\left\{-kT+\frac{\partial E}{\partial n_1}\right\}\right]\Big/V_fJ_{1l}. \tag{67}$$

[32] Guggenheim, Fowler's *Statistical Mechanics*, second edition (1936), p. 528.

Using Eq. (57) for V_f, the partial pressure is expressed in terms of the internal pressure of the liquid.

$$p_1=N_1\frac{J_{1_0}kTp_i^3}{J_{1_i}V_{f1}^0p_{1_i}^{03}}\exp\left[3(n_1+n_2)\frac{\partial\log p_i}{\partial n_1}-\frac{1}{kT}\left\{kT-\frac{\partial E}{\partial n_1}\right\}\right]. \tag{68}$$

From this equation, the conditions for ideal solutions are apparent, i.e., the internal pressure and the partial molal internal energy must be independent of mole fraction. In order to examine the deviations from Raoult's and Henry's laws it is convenient to expand p_1 in powers of N_2 for small concentrations of component two. Setting $p_i=a/V^2$ and $E=-(n_1+n_2)/N(a/V)$, (68) becomes:

$$p_1=N_1(p_1)_{N_2=0}[1+N_2^2\{A+(a_1/V_1RT)B\}+N_2^3\{\cdots\}+\{\cdots\}+\cdots], \tag{69}$$

where
$$A\equiv-3\left[\alpha_2-\tfrac{1}{2}\alpha_1^2-\frac{1}{V}\frac{\partial^2V}{\partial N_2^2}+\frac{1}{V^2}\left(\frac{\partial V}{\partial N_2}\right)^2\right]_{N_2=0} \tag{70}$$

and
$$B\equiv\tfrac{1}{2}\left(\frac{\partial^2}{\partial N_2^2}\frac{a}{V}\right)_{N_2=0}=\left[\alpha_2-\frac{\alpha_1}{V}\frac{\partial V}{\partial N_2}-\frac{1}{2V}\frac{\partial^2V}{\partial N_2^2}+\frac{1}{V^2}\left(\frac{\partial V}{\partial N_2}\right)^2\right]_{N_2=0.} \tag{71}$$

Here A and a_1B/V_1RT are the first deviation from Racult's law due to the nonideality of the entropy and energy respectively. A and B are completely determined from (51) and (52). These quantities assume a particularly simple form when $a_1/V_1RT=10$, which corresponds to a temperature near the boiling point for liquids which obey Trouton's rule. For such a temperature:

$$\begin{aligned}A&=-3/4[8\alpha_2-12\beta_2+\beta_1^2-9\alpha_1^2+10\alpha_1\beta_1],\\ B&=3/2(\alpha_2-\beta_2)-\alpha_1\beta_1-(1/4)\alpha_1^2+(5/4)\beta_1^2.\end{aligned} \tag{72}$$

So that for this temperature

$$\begin{aligned}A+(a_1/V_1RT)B=3/4[&2(\alpha_2+\beta_2)\\&+49\beta_1^2-\alpha_1^2-50\alpha_1\beta_1].\end{aligned} \tag{73}$$

In examining these formulae, it may be useful to remember that

$$\begin{aligned}\alpha_2&=[a_2+a_1-2a_{12}]a_1^{-1},\\ \alpha_1&=2a_1^{-1}[a_{12}-a_1],\end{aligned} \tag{74}$$

and similarly for β_1 and β_2. It will be noticed that A and B are functions of the temperature and their temperature variation could be determined by taking the derivatives of (70) and (71). Therefore the variation of the deviation from Raoult's law with temperature would be an interesting property to compare theory and experiment. The four constants a_1, a_2, b_1, b_2 are known with reasonable accuracy for most substances but the interaction terms a_{12} and b_{12} are difficult to estimate. The comparison of the experimental and theoretical properties of solutions should first serve in the evaluation of a_{12} and b_{12} before checking the applicability of our model or assumptions.

Osmotic Pressure

The osmotic pressure of a binary mixture[33] is related to the free energy by the thermodynamical relationship:

$$(\partial F/\partial n_1)_{n_2,\ p+P}=(\partial F/\partial n_2)_{n_2=0,\ p}. \tag{75}$$

Here P is the osmotic pressure and p is the external pressure. Using (66) Eq. (75) becomes

$$\begin{aligned}P\bar{V}_1+p(\bar{V}_1-V_1^0)+(E_1-E_1^0)=\\ -RT\log(N_1v_{f1}^0/v_{f1}).\end{aligned} \tag{76}$$

In this equation $\bar{V}_1$ is the partial molal volume at a pressure $(P+p)$ which can be computed from Eq. (47);

$$E_1=-2(a/V)+\bar{V}_1(a/V^2)+(N_2/V)(\partial a/\partial N_2);$$

and the quantities E_1^0 and V_1^0 are the molal energy and volume respectively of the pure solvent at pressure p. From Eq. (56) it follows that

$$(v_{f1}^0/v_{f1})=[(p_{i1}+p_{ex1})/(p_{i1}^0+p_{ex1})]^3. \tag{77}$$

[33] Guggenheim, *A Commentary on the Scientific Writings of Willard Gibbs* (Yale University Press, 1936), Vol. I, p. 181; also Fowler's *Statistical Mechanics*, second edition (1936), p. 531.

We now take log $(p_{i_1}+p_{ex_1})$ to be a partial molal quantity satisfying a relation similar to (50) so that

$$(p_{i_1}+p_{ex_1})=(p_i+p_{ex})$$
$$\times\exp\left(-N_2(\partial/\partial N_2)\log(p_i+p_{ex})\right). \quad (78)$$

Therefore each term in Eq. (76) can be readily computed in terms of the a's and b's. Eq. (76) has the advantage over other equations for osmotic pressure in that it includes the compressibility terms in an integrated form.

An analogy between the osmotic pressure and the equation of state for gas has often been made. This analogy can be completed by considering the solvent molecules such that $a_1=a_{12}=0$. In this case:

$$(P+N_2^2a_2/V^2)\bar{V}_1=-RT\log(N_1v_{f_1}^0/v_{f_1}). \quad (79)$$

For dilute solutions, $v_{f_1}^0=v_{f_1}$ and $-\log N_1=N_2$. Setting:

$$\bar{V}_1=(V-N_2\bar{V}_2)/N_1. \quad (80)$$

It follows that

$$(P+N_2^2a_2/V^2)(V-N_2\bar{V}_2)/N_1N_2=RT. \quad (81)$$

But V is the volume of one mole of solution and the usual equations of state are in terms of the volume of one mole of the solute molecule $V'=V/N_2$. Now $\bar{V}_2$ is the additional volume which must be provided when a mole of molecules of type two are added to the liquid without changing the number of molecules of type one. Now this volume from which other molecules are excluded we take as b_2 and so obtain the van der Waals equation for a gas:

$$(P+a_2/V'^2)(V'-b_2)=RT. \quad (82)$$

We have here endowed our solvent with the properties of empty space or "holes." The equation of state for a liquid is obtained from (79) by slight modifications in the argument. The equation of state can thus be thought of as a particular case of the osmotic pressure equation for two component systems so that all of the arguments regarding critical phenomena of one component systems apply in an obvious way to binary systems.

Lower critical solution temperatures

Most of the binary systems which exhibit a lower consolute point are made up of substances capable of associating by means of hydrogen bridges. The phenomenon is particularly common among binary systems of which one component is water or alcohol, the other a derivative of ammonia. The upper critical solution phenomenon has been long understood but few if any theories have been advanced to explain the lower critical solution temperature.[34] The explanation we propose is the following. van der Waals' forces are comparatively long range and therefore do not depend on the relative orientation of neighboring molecules. When other forces act such as dipole-dipole, or valence forces like those present in hydrogen bridges the situation is more complicated. These other forces are effective only at short range and depend strongly on the relative orientation of the two molecules concerned. The lower critical solution temperature is then the temperature at which at least one of the components of the solution begins rotating. When this occurs the orientation necessary for the effective action of the short range forces is no longer present. If it is still true that one or both of the components in the pure form retains its bridge structure we expect the pure phases to have a considerably lower energy. This, however, is the condition required to make the potential energy high for the mixed system so that in spite of the entropy of mixing this will lead to a separation into two phases.

There is a definite analogy between this phenomenon and that of denaturation of proteins.[35] In each one probably has the breaking of hydrogen bridges with a gain of rotational freedom.

[34] Mertzlen, J. Gen. Chem. **5**, 161 (1935).
[35] Mirsky and Pauling, Proc. Nat. Acad. Sci. **22**, 439 (1936).

The Diffusion of Hydrogen Through Carbonyl Iron at Temperatures from 800° to 1100° Centigrade

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The diffusion of hydrogen through hydrogen-purified carbonyl iron shows breaks in the log (rate) *vs.* $1/T$ curve at 834, 909 (body-centered→face-centered phase change), 945, 1009, 1056, 1082 and 1103 deg. centigrade. These are average values for three samples of "Mehl" iron. The log (rate) *vs.* $1/T$ curves at these temperatures are composed of arcs, the above points being ends of these arcs. These points fall on a line whose slope is 4085 deg. Kelvin. Thus b in the expression $\exp(-b/RT)$ is given as 18,680 cal./g atom for these points. The above temperatures belonging to the ends of the arcs can be fitted to a Balmer type formula, i.e., $T(°K)=C(1/3^2-1/n^2)$, where $n=6, 7, 8, \cdots$, and $C=13{,}430\pm30$ for the breaks starting with $n=7$, while $C=13{,}301$ for the break with $n=6$. This difference is presumably caused by the $n=6$ break being in the body-centered phase, while all breaks starting with $n=7$ are in the face-centered phase.

DURING the past year we have developed the experimental technique previously reported by one of us[1] in order to study the diffusion of gases through metals at high temperatures. These studies, at the present time, are concerned with the diffusion of hydrogen through iron and nickel, especially the former element. We have investigated the diffusion of hydrogen through iron from 60° to 1100° centigrade,[2] in steps of 5 to 10 degrees, and it will be obvious that with precision technique, the state of affairs represented by the previous conclusions derived from data on iron is far from the truth. When only a few points are taken on the isobars, most of the important characteristics are apt to be attributed to experimental error.

Borelius and Lindbloom,[3] Ryder,[4] and more recently, Smithells and Ransley[5] have studied the diffusion of hydrogen through iron at temperatures ranging from 245° to 780° centigrade. The data presented by these authors is in a region in which the diffusion is fairly regular, consequently they have drawn straight lines through their $\log D$ *vs.* $1/T$ plots in order to determine the work function b in the expression[6]

$$D=AP^{\frac{1}{2}}T^{\frac{1}{2}}\exp(-b/RT), \qquad (1)$$

where D is the rate of diffusion measured in grams of hydrogen diffusing through unit area per mm thickness at the temperature T, and A is a constant of proportionality. Eq. (1) assumes that the pressure P is exerted by the gas on one side of the diffusing material and a vacuum is maintained next to the outgoing face.

Smithells and Ransley[5] have shown quite clearly that the diffusion of hydrogen through iron takes place *through* the lattice. Their experiment consisted in showing that the diffusion through iron gave the same rate for a single crystal as for a polycrystalline sheet. The familiar $P^{\frac{1}{2}}$ relationship for pure metals, as given by Eq. (1), suggests that the hydrogen goes through the lattice in the atomic form.[6, 7] Fowler[8] has considered the solution of gases in metals by assuming the gas to be present in the metal as protons and electrons.

We have found that every important structural, or phase change, in the sample under investigation can be recognized by the diffusion rates. Thus the Curie region in pure iron and nickel can be recognized. Since this region is not distinguished by a change in crystal structure, but is to be accounted for by changes in the electronic structure of the iron lattice,[9] we must conclude that the rate of diffusion of hydrogen through iron and nickel is intimately connected

[1] W. R. Ham, Am. Soc. Metals, **25**, 536–564 (1937).
[2] Mr. W. L. Rast will shortly publish his data on the lower temperature runs for "Mehl" iron.
[3] Borelius and Lindbloom, Ann. d. Physik **82**, 201 (1927).
[4] Ryder, Elec. J. **17**, 161 (1920).
[5] Smithells and Ransley, Proc. Roy. Soc. **A150**, 172 (1935).
[6] Richardson, Nicol and Parnell, Phil. Mag. **8**, 1–29 (1904).
[7] Donnan and Shaw, J. Soc. Chem. Eng. **29**, 987 (1910).
[8] R. H. Fowler and C. J. Smithells, Proc. Roy. Soc. **A160**, 37 (1937).
[9] J. C. Slater, Phys. Rev. **49**, 537 (1936); ibid. **49**, 931 (1936).

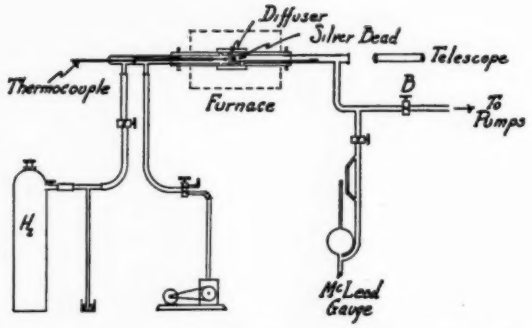

FIG. 1. Apparatus for "steady-state" and trapping methods.

to the electric fields surrounding the lattice points.

A change in crystal structure can be recognized very clearly. The body-centered to face-centered phase change in pure iron is easily recognized, in fact, the rate of diffusion is halved in passing from the body-centered to the face-centered form. In all probability, the change in rate of diffusion between these two structures is due to the interaction of the hydrogen ion, or atom, with the field. Although the detection of these electronic and structural changes does not prove definitely which of the two forms, atomic or ionic, exists in the diffusion of gases through metals, we feel that to account for the magnitude of the change in rates we must assume the ionic form for hydrogen as it passes from point to point of the lattice. The hydrogenic electrons will presumably become a part of the free electrons of the metal, as suggested by Fowler.[8]

In addition to the above arguments for the ionic form, we have found a new temperature effect for the diffusion of hydrogen through iron which is definitely outside the limit of our experimental error. When the high temperature data is plotted in the form of log (rate) *versus* $1/T$, we find that the curve is composed of arcs, the end points of the arcs being characteristic of hydrogen through iron. The temperatures of the end points of these arcs can be fitted to a Balmer type formula, where the constant "term-value" belongs to the number 3. We have followed this series up to the temperature 1103° and although there is indication that further breaks lie above this temperature, we cannot resolve the breaks sufficiently to fix, experimentally, the running coordinate n in the formula.

EXPERIMENTAL PROCEDURE

A detailed description of the apparatus is to be found elsewhere,[1] but we will give a short description of the apparatus and a detailed description of the experimental procedure used here to establish the validity of the results. Fig. 1 is a schematic drawing of the necessary equipment needed for the steady-state, and trapping, methods.

The essence of the "steady-state" method lies in having the stopcock B barely open to the pumps. A small back pressure (10 to 60 microns, i.e., 10^{-4} cm Hg) is obtained which can be read on a McLeod gauge. When the opening through the stopcock B is very small a larger pressure is obtained. This we designate as "increasing the sensitivity." The sensitivity will be given as the ratio of the pressure when the cock B is barely open, to the rate (as read on the gauge) when the cock is entirely open to the pumps. It is necessary that the McLeod gauge be as accurately calibrated as possible and then recorrected by timing the build-up in pressure when only a small amount of gas is being trapped by diffusion through the sample.

That the steady-state method gives consistent results with the trapping methods is shown in Fig. 2. Here we have plotted the log of the rate as determined by the trapping method against the log of the steady state rate. This graph is important because of the fact that previous investigators have used the trapping method. The diffusion rate of hydrogen through iron and nickel at high temperatures is relatively high

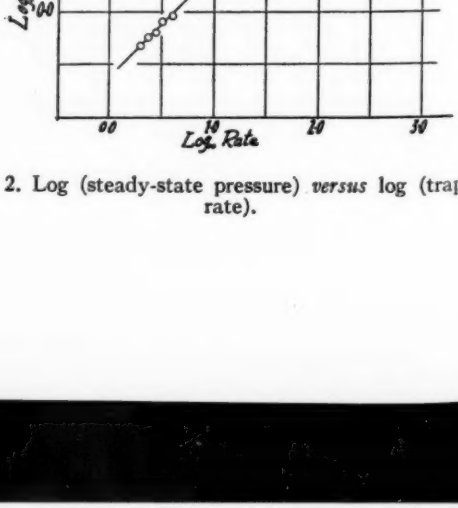

FIG. 2. Log (steady-state pressure) *versus* log (trapping rate).

unless reduced pressures are used on the ingoing side of the diffuser. Reducing the pressure is valid for a small number of points, but since we take readings every 5 degrees at these temperatures we find that more accurate results can be obtained by keeping the ingoing pressure at atmospheric conditions and then correcting the rates by the $P^{\frac{1}{2}}$ law to 760 mm Hg. Fig. 2 shows that the two rates are directly proportional to one another.

Figure 3 is a detailed sketch of the diffusers used and the type of assembly. Diffuser (1) was made by welding with atomic hydrogen the "Mehl" iron[10] disk to a nickel tube. After machining to the desired thickness this outside nickel tube was atomic hydrogen welded to smaller nickel tubes. The wall thickness of these nickel tubes was 3/16 inch. Water coolers were placed at the ends for deKhotinsky joints to the vacuum system and hydrogen inlet. This type of diffuser was abandoned after one trial because of nickel contamination in the welding. The baffle plates of pure iron were to protect the diffuser when the ends were welded to the sample holder. Diffuser (2) has been the most successful of the types made to date. The iron disk was atomic hydrogen welded to two pieces of Armco iron tubing. This tubing had been previously baked for 50 hours at 1100°C in hydrogen for the purpose of removing most of the carbon present in this low carbon iron. The baffle plates were then inserted and the inside unit gold (or copper) welded to the outside nickel tube. All of these operations were carried out with a hydrogen atmosphere next to the diffusing disk. The ends were then atomic hydrogen welded to the whole central unit after the disk had been machined to the desired thickness (usually 60 to 80 mils for high temperature diffusion studies).

The furnace was thermostated by means of a photoelectric cell circuit. The controlling thermocouple was placed next to the heating coils in the furnace. The heating coils were separated from the diffusing tube by about 3/8 inch of porcelain. This position of the controlling couple gave exceptionally good results because the proximity of the couple to the heating coils enabled the circuit to completely control the temperature at the center of the heating coils. Since these coils were so near the diffusing tube, the temperature of the diffusing disk remained constant over any length of time desired.

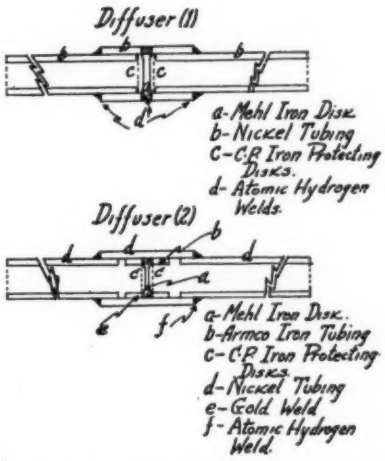

FIG. 3. Diffuser assembly for Mehl iron samples.

The temperatures of the disk were read by means of a chromel-alumel thermocouple, size 18 wire, inserted in through the hydrogen end and placed 1 mm distant from the disk. This wire had been standardized by the National Bureau of Standards.[11] In order to make sure that the couples were not drifting with time we would check them before and after a run by means of the melting point of 99.98 percent purity silver as follows. A small bead of this silver was placed on an iron holder. This holder was connected to a piece of nickel by means of a lightweight Nichrome wire. The nickel piece protruded from the nickel tube of the diffuser to such a distance that it could be manipulated by magnets. The holder was then slid up against the disk and the melting point ascertained by means of visual observation through the telescope shown in Fig. 1. The thermocouples are thus standardized while in the position they occupied during the run.

The temperatures recorded by the inside couple were read by means of a Leeds and Northrup type K potentiometer using a galvanometer with a current sensitivity of 2.72×10^{-6} amp./mm

[10] We must express our thanks to Dr. F. R. Mehl of the Carnegie Institute of Technology for furnishing us with a supply of his hydrogen purified carbonyl iron. This carbonyl iron was purified by baking at 1100°C in an atmosphere of purified hydrogen. For a description of this iron see reference 13.

[11] We wish to thank Mr. Roesser of the National Bureau of Standards for furnishing us this thermocouple wire and standard silver beads.

deflection. The galvanometer resistance was 4.4 ohm. The thermostat held the temperature constant to *less* than 1/4 mm deflection on the potentiometer galvanometer. This means that the temperature was constant to within ± 0.07 degrees at temperatures up to 1125°C.

Leak tests were run by substituting helium for hydrogen. The leak test in all of these runs amounts to only about 2 percent of the recorded rate. The readings were corrected to take account of this leak rate. At the beginning of a run the diffuser was taken to a temperature about 25 degrees above the highest recorded temperature used for a rate reading. The diffuser was held at this temperature (usually 1125 deg. C.) with the pumps and hydrogen on for about an hour. The rate would then be lowered in small steps of about 5 to 10 degrees to about 875°C. The rate would then be read as the temperature was raised back to the starting temperature. At these temperatures a steady state is reached in about 10 minutes. In all cases, readings of the pressure would be taken until a duplicate reading was obtained. Considerable trouble was experienced in obtaining complete runs of this kind because of the nichrome winding of the furnace failing at these high temperatures. Several complete runs were obtained in addition to much data over limited regions.

All of the results up to 1000 deg. C reported here have been checked by different observers and two other sets of apparatus at this laboratory.

Experimental Results

Figure 4 is a direct plot of the diffusion rate of hydrogen through Mehl carbonyl iron against the temperature in millivolts (uncorrected).[12] The corrected temperatures are clearly indicated at the breaks. It is unfortunate that a low sensitivity was used in Fig. 4, otherwise the breaks at 955° and 1010° would show to better advantage when plotted to this small scale. The higher breaks are clearly defined at this sensitivity. It is significant that the $\gamma \rightarrow \alpha$ phase change, which normally occurs at 910°C for this type of iron,[13] has been supercooled to 856°C when the sample is brought in these small steps from 1125°C. A repeat run with a technique to be discussed in a later paper on the rates of transformation of this phase change, shows the $\gamma \rightleftharpoons \alpha$ transformation to occur at 890°.

Figure 5 shows the breaks at 951° and 1014° for another sample. This run was made at a higher sensitivity than Fig. 4 and the lower breaks are clearly defined. Fig. 5 also illustrates the type of diffusion break found at the crystal structure change.

Figure 6 shows the rate of diffusion of hydrogen through a sample contaminated with nickel. This diffuser was of the first type described. Each of the "break" points has been lowered in a regular manner and also decreased in intensity. We will shortly publish some data on the diffusion of hydrogen through nickel, and we can anticipate this publication by saying that such a series of breaks as is found here in pure iron has not been found in nickel.

Figure 7 shows the appearance of these breaks when the log of the steady state rate is plotted against $1/T$, where T is in degrees Kelvin. The deviation of the curved lines from the dashed straight line are definitely outside the range of experimental error. Furthermore, if an error in

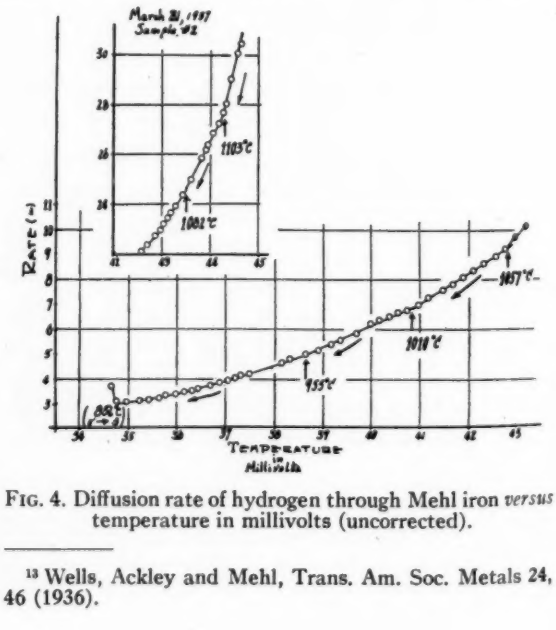

FIG. 4. Diffusion rate of hydrogen through Mehl iron *versus* temperature in millivolts (uncorrected).

[12] All of the data shown in this paper was plotted after the readings were taken. No objection should be raised to plotting the temperature as millivolts in Figs. 4, 5, and 6 because the features we wish to point out in these curves are the breaks. The National Bureau of Standards thermocouple wire used here was selected because of its linear relationship between e.m.f. and temperature. The corrected temperatures of the breaks are clearly indicated.

[13] Wells, Ackley and Mehl, Trans. Am. Soc. Metals 24, 46 (1936).

the apparatus caused the deviations, it would certainly be expected that the deviations would be erratic. This latter point bears more weight when it is considered that the points shown on the graphs represent only one out of three or four points. This is necessary because of the difficulty of drawing small graphs so that they may be legible. The straight line which can be drawn through each of the "breaks" in Fig. 7 has a slope of 4085 abs. deg., hence b in the expression

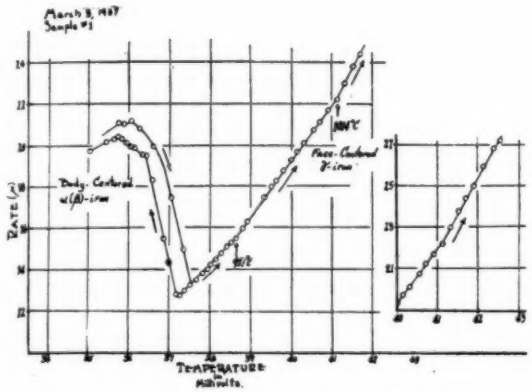

FIG. 5. Diffusion rate of hydrogen through Mehl iron *versus* temperature in millivolts (uncorrected).

$\exp(-b/RT)$ is 18,860 cal./g atom for these points.

The data obtained for the temperature of the body-centered to face-centered phase change are not to be trusted in view of the excellent determination of this point recently made by Wells, Ackley and Mehl.[13] The chances for slight contaminations at high temperatures are too great to record our temperatures of the $\alpha \rightleftarrows \gamma$ transformation as belonging to pure iron. Slight contaminations will lower this point in a surprising manner which can be accounted for by use of the Van't Hoff freezing point lowering formula. Austin[14] gives $\Delta H = -218$ cal./g atom as the heat effect at the transition, $T = 1183°$K, whence 1.27×10^4 is the lowering of the phase change temperature in the infinitely dilute solution, per mol of impurity in one gram atom of iron, providing the impurity is insoluble in the body-centered phase. While these small amounts of contamination make our results inaccurate for the determination of this temperature, nevertheless we feel that small amounts of contaminant do not effect appreciably the location of the breaks given above excluding, of course, the body-centered face-centered transformation. Table I bears out this latter conclusion. Here we list the temperatures obtained for these breaks from three different samples. The temperatures of the breaks up to, and including 1014 have been obtained many times on samples which were not taken to higher temperatures. The sample which shows the breaks lowered appreciable amounts (Fig. 6) is obviously heavily contaminated with nickel.

[14] J. B. Austin, Eng. Ind. Chem. **24**, 1225 (1932).

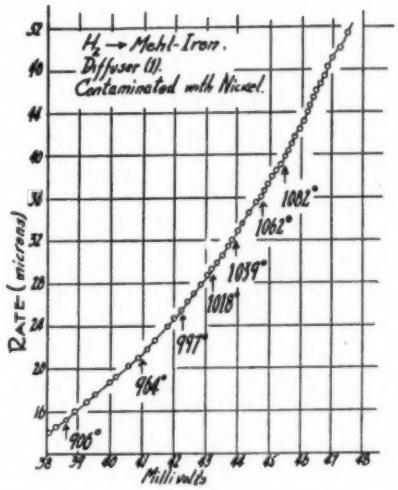

FIG. 6. Diffusion of hydrogen through Mehl iron contaminated with nickel.

DISCUSSION OF RESULTS

Ham[1] previously noted the existence of the 835 and 945 degree breaks, both in iron obtained from Yensen, of the Westinghouse Laboratories, and in Mehl iron. He also suspected the existence of the break at 1010 degree cent., but he did not take his samples to a high enough degassing temperature to be sure of this latter break. This would indicate that the existence of this series is not alone limited to Mehl iron, in fact we may say, that this series should be characteristic of all pure carbonyl iron which has been purified so that it approaches closely the purity of pure iron.

At this time we wish to recapitulate the following pertinent points: (1) That our temperature control is good to within ± 0.07 degrees for all temperatures recorded here, (2) That the previ-

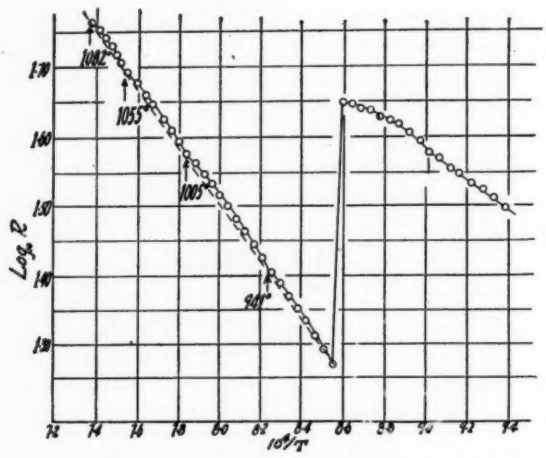

FIG. 7. Log R *vs.* $1/T$ for hydrogen through Mehl iron.

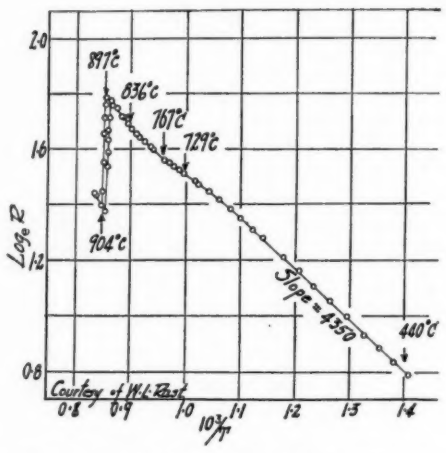

FIG. 8. Log R *vs.* $1/T$ for carbonyl iron for temperature range 440° to 925°C.

ously standardized inside thermocouple was rechecked at the melting point of 99.98 percent purity silver while in the position it occupied during the runs, (3) That the precision of the pressure readings is limited only by the accuracy of reading the McLeod gauge (this error on Fig. 7 amounts to less than half the width of the circles drawn there), (4) That the breaks up to, and including, the temperature 1012° were previously shown in graphs by Ham,[1] and that these breaks up to 1012° have been checked by different observers on two other sets of apparatus during the past year, (5) That equilibrium was reached in all these readings as shown by the fact that the same temperature was held until a duplicate reading was obtained for the diffusion rate before moving on to the next temperature, (6) That Figs. 4 and 5 represent the general characteristics of these breaks and that the abruptness of the change in slope can be controlled somewhat by the sensitivity of the apparatus (see "Experimental Procedure"), and (7) that we have obtained limited runs throughout this region which is in agreement with Figs. 4, 5, and 7, but which are not shown because of lack of space.

We early sought for a series which would express these experimentally determined points. These breaks were found to fit a Balmer type formula. We find it necessary to give the number 3 to the fixed "term-value," consequently n, the running coordinate, will take the values 6, 7, 8, ···. This series, with its constant, is as follows:

$$T(°\mathrm{K}) = (13{,}430 \pm 30)(1/3^2 - 1/n^2). \qquad (2)$$

Table II gives the temperatures, the values of n, and the constant computed from the experimental data. The average value with its deviation is 13,430±30 for the breaks starting with $n=7$. The first value was not averaged with the following because we feel that it should be different from the others for the obvious reason that the first break lies in the body-centered phase, while all the others lie in the face-centered. If this series is connected in any way with the interplay of forces between the hydrogen ion and the electric fields surrounding the iron lattice, then we would expect the forces to be different for the iron in the body-centered form and in the face-centered form.

TABLE I. *Temperature of breaks in diffusion curves, hydrogen through iron.*

Sample No. 1	835	955	1010	1057	1082	1103
Sample No. 2	833	941	1005	1055	1082	——
Sample No. 3	836	951	1014	——	——	——

TABLE II. *Determination of constants in series for experimental breaks.*

TEMP. (°K)	n	CONSTANT	DEVIATIONS
1108	6	13301	——
1222	7	13472	+42
1283	8	13434	+ 4
1329	9	13455	+25
1355	10	13403	−27
1376	11	13385	−45

Average Constant = 13430±30

That the diffusion of hydrogen through iron does not follow the simple relation expressed by Eq. (1), except over limited regions, is shown by Fig. 8. Here we show the log (rate) *vs.* $1/T$ for a sample of Mehl iron in the range from 925° to 300°C. Mr. W. L. Rast will shortly publish his data on these low temperature runs and discuss them in detail, in addition to discussing the anomalous behavior of hydrogen through iron below 300°. In the meantime we are indebted to Mr. Rast for allowing us to reproduce Fig. 8.

This graph also makes it clear why previous investigators only reported the range of diffusion from about 750 to 300°C. This region does correspond, to a first approximation, to Eq. (1), and if only a few points were taken it is clear that one would think that the log (rate) *vs.* $1/T$ curves should be linear. The general features of Fig. 8 have been consistently obtained for pure iron over a period of several years. These observations have been made by different observers and three different sets of apparatus.

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The Crystal Structure of Potassium Metaborate, $K_3(B_3O_6)$

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(Received August 23, 1937)

In order to find the configuration of the metaborate group the crystal structure of potassium metaborate was determined. The crystals are rhombohedral $a_r=7.76$A, $\alpha=110°\,36'$ with six molecules KBO_2. The density is 2.348. The space group is $R\bar{3}c(D_{3d}^6)$. All atoms are lying on twofold axes at positions: $\pm(u, \frac{1}{2}-u, \frac{1}{4})$ ↻. The parameters were determined by means of two-dimensional Fourier analyses:

K $u=0.689\pm0.003$, B $u=0.361\pm0.006$,
O_I 0.465 ± 0.006, O_{II} 0.146 ± 0.006.

The metaborate radical is $(B_3O_6)^{-3}$, a ring of three BO_3 triangles, rather than the endless chain of BO_3 triangles found in CaB_2O_4. The BO_3 groups are slightly distorted, the B–O distances being 1.33A, 1.38A and 1.38A, the O–O distances 2.30A, 2.38A and 2.38A. The nine particles of the radical lie in one plane. Potassium is surrounded by seven oxygen atoms at a distance 2.82A.

A FEW years ago we investigated the crystal structure of calcium metaborate, $Ca(BO_2)_2$,[1] and found that it contained the metaborate groups as endless chains built up of BO_3 triangles. While our studies of the borates have convinced us of the nonexistence of radicals $(BO_2)^-$, we considered it likely that the metaborate group in some crystals occurs in a state of finite polymerization, namely as rings of BO_3 triangles. The reported symmetry and optical properties of $NaBO_2$ and KBO_2[2] indicated that possibly such ringshaped metaborate groups might be present in these crystals, and an x-ray investigation was therefore undertaken. This article contains a discussion of the results obtained for KBO_2.

Excellent crystals of KBO_2 were prepared by melting together K_2CO_3 and B_2O_3 in a platinum crucible. The melt was cooled rapidly so that a crust formed on the outside. In the cavity thus produced in the interior needleshaped hexagonal crystals (up to two cm long) were found. The density was determined by the suspension method (using methylene iodide and toluol) to 2.348 ± 0.005. The crystals are hygroscopic and were kept in minute desiccators during the x-ray exposures.

The crystals were examined by the oscillation and Laue methods. The oscillation photographs were taken with copper radiation filtered through a nickel film.

For the dimensions of the hexagonal cell we found:

$$a=12.75\pm0.02\text{A}, \quad c=7.33\pm0.04\text{A}.$$

However, the true unit cell is rhombohedral and has dimensions:

$$a_r=7.76\text{A}, \quad \alpha=110°\,36'.$$

It contains six (5.98) molecules KBO_2.

[1] W. H. Zachariasen, Proc. Nat. Acad. **17**, 617 (1931); W. H. Zachariasen and G. E. Ziegler, Zeits. f. Krist. **83**, 354 (1932).
[2] S. S. Cole, S. R. Scholes, C. R. Amberg, J. Am. Ceram. Soc. **18**, 58 (1935).

The Laue photographs as well as the oscillation photographs showed the symmetry characteristic of the point group $\bar{3}m(D_{3d})$. Accordingly the following space groups come into consideration: $R3m(C_{3v}^5)$, $R3c(C_{3v}^6)$, $R32(D_3^7)$, $R\bar{3}m(D_{3d}^5)$ and $R\bar{3}c(D_{3d}^6)$. Reflections HHL (the Miller indices used throughout the article refer to the rhombohedral cell) are absent if L is odd. This fact indicates that $R3c$ or $R\bar{3}c$ is the space group.

The structure was deduced by methods of Fourier analysis. The positions of the potassium atoms were found from a two-dimensional Patterson analysis (projection plane normal to the 3-fold axis), in which the outstanding peaks must be attributed to potassium-potassium vectors. To find the positions of boron and oxygen atoms an ordinary two-dimensional analysis was next made, using the known potassium contribution to obtain the probable signs of the coefficients in the series. Finally the electron density variation was evaluated along one of the twofold axes.

The structure so obtained is as follows: Space group $R\bar{3}c$. All atoms are lying on twofold axes at positions: $\pm(u, \frac{1}{2}-u, \frac{1}{4})\circlearrowright$. The parameter values are:

	$2\pi u$	u
K	248° ±1°	0.689±0.003
B	130 ±2	.361± .006
O_I	167.5±2	.465± .006
O_{II}	52.5±2	.146± .006

The observed intensities and calculated amplitudes for a number of reflections are given in Table I.

Figure 1 shows a projection of the structure on a plane normal to the 3-fold axis. Each potassium atom is surrounded by seven oxygen atoms, one O_I at a distance of 2.85A, two O_I at 2.80A, two O_I at 2.83A and two O_{II} at 2.81A. The average value, 2.82A, agrees with the predicted value of 2.85A for coordination number seven.[3]

Each boron atom is linked to three oxygen atoms forming a nearly equilateral triangle with edges 2.30A($O_{II}-O_{II}$), 2.38A(O_I-O_{II}) and 2.38A(O_I-O_{II}). The boron to oxygen distances are nearly equal 1.33A($B-O_I$) and 1.38A($B-O_{II}$). The same average dimensions of

[3] W. H. Zachariasen, Zeits. f. Krist. **80**, 137 (1931).

TABLE I. *Oscillation photographs around [111].*[1]

HKL	sin θ/λ	Int. obs.	|F| calc.	HKL	sin θ/λ	Int. obs.	|F| calc.	HKL	sin θ/λ	Int. obs.	|F| calc.	HKL	sin θ/λ	Int. obs.	|F| calc.
$1\bar{1}0$	0.078	nil	1	$2\bar{1}0$	0.138	*vw*	20	110	0.144	*m*	42	210	0.219	*wm*	51
$2\bar{1}\bar{1}$	.136	nil	6	$21\bar{2}$	.177	*m.*	71	200	.164	*s*	87	$3\bar{1}1$	.258	nil	0
$22\bar{0}$	.157	*vw*	20	$32\bar{0}$	.209	*wm*	35	$21\bar{1}$	.182	*w−*	20	$4\bar{1}0$	.291	*wm*	30
$32\bar{1}$	.208	*vw*	11	$31\bar{3}$	.249	*wm*	42	$3\bar{1}0$	.213	*m−*	40	$32\bar{2}$	.291	*wm*	30
$33\bar{0}$	.235	*s*	70	$42\bar{1}$	.261	*ms*	44	$22\bar{2}$	.227	*wm*	34	$41\bar{2}$	.312	*w−*	26
$42\bar{2}$	.272	nil	6	$43\bar{0}$	.284	*w.*	35	$31\bar{2}$	.240	*tr*	4	$52\bar{0}$	.349	nil	6
$43\bar{1}$	.282	*w.*	28	$32\bar{4}$	.305	nil	6	$4\bar{1}\bar{1}$	.264	*s*	54	$42\bar{3}$	.349	nil	6
$44\bar{0}$	.314	*w*	31	$41\bar{4}$	.324	*m−*	35	$42\bar{0}$	.276	*w−*	20	$51\bar{3}$	.375	*wm*	48
$53\bar{2}$	.342	*vw*	16	$53\bar{1}$	.334	*vw.*	16	$32\bar{3}$	.287	*w*	29	$62\bar{1}$	.398	*w*	25
$54\bar{1}$	.359	nil	5	$54\bar{0}$	.360	nil	7	$41\bar{3}$	.307	*vw*	13	$43\bar{4}$	.398	*w*	25
$55\bar{0}$	.392	*vw−*	10	$42\bar{5}$	.377	nil	9	$52\bar{1}$	.327	*w−*	20	$63\bar{0}$	.414	*vvw*	7
$63\bar{3}$	.408	*s*	89	$63\bar{2}$	.393	*vw*	20	$33\bar{4}$	.345	*m.*	58	$52\bar{4}$	.414	*vvw*	7
$64\bar{2}$	.415	nil	4	$51\bar{5}$	.401	*m*	44	$53\bar{0}$	.345	*w.*	30	$61\bar{4}$	.442	*w*	20
$65\bar{1}$	.437	*vw*	15	$64\bar{1}$	.408	nil	6	$42\bar{4}$	.354	*w−*	11	$73\bar{1}$	.463	*w*	27
$66\bar{0}$	.463	*wm*	39	$43\bar{6}$	.437	*vw−*	6	$51\bar{4}$	.379	*w.*	28	$53\bar{5}$	.463	*w*	27
$74\bar{3}$	.477	nil	3	$65\bar{0}$	.437	*w−*	24	$62\bar{2}$	.387	*vw−*	1	$74\bar{0}$	.482	nil	0
$75\bar{2}$	.490	nil	8	$52\bar{6}$	.451	*w*	19	$63\bar{1}$	.395	*m−*	49	$62\bar{5}$	.482	nil	0
				$74\bar{2}$	.465	nil	9	$43\bar{5}$	.410	*vw*	5				
				$61\bar{6}$	.478	*vw*	10	$64\bar{0}$	.418	*w−*	22				
				$75\bar{1}$	.484	*w*	36	$52\bar{5}$	.425	*vvw*	3				
								$73\bar{2}$	.453	*vw.*	20				
								$61\bar{5}$	.453	*vw−*	4				
								$74\bar{1}$	.466	*vw.*	18				
								$44\bar{6}$	.473	*w*	30				
								$53\bar{6}$	.479	*m*	44				
								$75\bar{0}$	.492	nil	8				
								$62\bar{6}$	.498	*w*	23				

[1] The scale of intensities is: *s, s−, ms, m., m, m−, wm, w., w, w−, vw., vw, vw−, vvw, tr.*
The *f* curves of James and Brindley were used in the calculations. All reflections up to sin θ/λ = 0.63 were measured. This table includes only reflections for which $H+K+L \leq 3$ up to sin θ/λ = 0.50. The amplitudes have been calculated using the parameter values 247.5°, 127.5°, 165°, 52.5° which are slightly different from the correct ones.

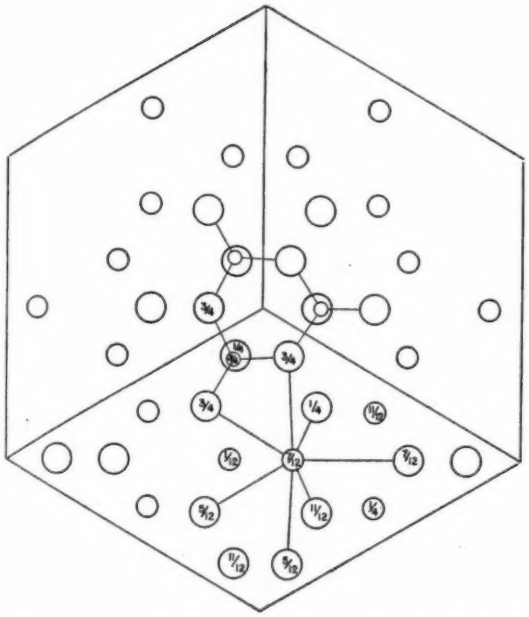

FIG. 1. A projection of the structure on a plane normal to the threefold axis. Only some of the atoms are shown; the remaining ones may be located by symmetry considerations. Large circles represent oxygen atoms, medium sized circles potassium and small circles boron atoms. Attached numbers give heights of atoms above plane of projection, expressed as fractions of cell diagonal (7.33A). The figure is bounded by the projected rhombohedral edges.

the BO_3 configuration have previously been found in other crystals.[4] An oxygen atom of the first kind (O_I) is thus linked to one boron and five potassium atoms, while an oxygen atom of the second kind is linked to two boron and two potassium atoms. The total bond strengths are 1.71 and 2.29, respectively. The angle between the two bonds $B-O_{II}$ is $126\frac{1}{2}°$ at the oxygen atom and $113\frac{1}{2}°$ at the boron atom.

Three BO_3 triangles are linked together by shared corners to form radicals $(B_3O_6)^{-3}$, the structure of which is shown in Fig. 2. All the nine atoms of the radical lie in the same plane, normal to the threefold axis. The observed strong negative birefringence ($\omega=1.526$, $\alpha=1.450$, Cole, Scholes, Amberg, reference 2) is thus simply accounted for.

The structure of the $(B_3O_6)^{-3}$ radical may be interpreted either in terms of ionic bonds or in terms of covalent bonds. Using the concept of

[4] For example: 1.35A in Be_2BO_3OH, W. H. Zachariasen, Zeits. f. Krist. **76**, 289 (1931); 1.36A in $Ca(BO_2)_2$, reference 1.

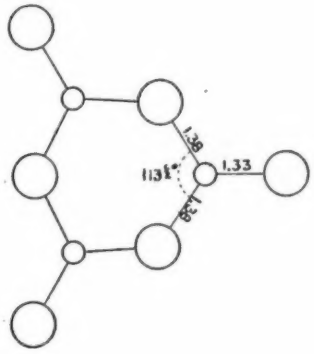

FIG. 2. The structure of the $(B_3O_6)^{-3}$ radical. Boron to oxygen distances are given in A.

covalent binding there would be resonance between the following three electronic structures:

The observed interatomic distances show, however, that the first of these three electronic structures is somewhat more important. The deformation within the BO_3 triangles may, on the other hand, equally well be explained by the repulsion between boron ions in the ionic interpretation.

In the calcium metaborate structure which we examined some years ago, the metaborate group does not occur in the form of a radical as in KBO_2; but rather as an infinite chain of BO_3 triangles. All the atoms of one such chain were found to lie approximately in one plane. (This is probably due to the resonating double bond.) We must emphasize the important result that in both calcium- and potassium-metaborate polymerization of the metaborate group has taken place rather than a reduction in the coordination number from three to two. Recently Rud Nielsen and Ward[5] have claimed that aqueous solutions of $NaBO_2$ contain radicals $(BO_2)^-$ built like CO_2. We consider this result highly improbable. It is quite possible that the $(B_3O_6)^{-3}$ radicals would break up when $NaBO_2$ enters into solution; but even if this be the case, one cannot expect radicals $(BO_2)^-$. In the presence of the oxygen atoms of the water molecules boron would certainly tend to be surrounded by as many

[5] J. Rud Nielsen and N. E. Ward, J. Chem. Phys. **5**, 201 (1937).

oxygen atoms as is sterically possible, i.e. boron would either be in a triangular or a tetrahedral configuration of oxygen atoms (respectively hydroxyl groups).

It may be of interest to point out the analogy which exists between metaborates and metasilicates (to a certain extent between borates and silicates in general). The metasilicates too show polymerization to retain the proper coordination number of four for silicon. The diopside chain corresponds to the (BO_2) chains of CaB_2O_4, while the three-membered ring of benitoite, $BaTiSi_3O_9$, corresponds to the $(B_3O_6)^{-3}$ radical of KBO_2. It is probable that some borates contain radicals $(B_4O_8)^{-4}$ analogous to the four rings of SiO_4 tetrahedra occurring in some silicates.

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Bimolecular Association Reactions

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The recent classical treatment of the rates of bimolecular association reactions proposed by Kimball is extended, and found to involve an essentially different dependence of reaction probability on vibrational energy initially present in the natural coordinates as kinetic energy from that present as potential energy. Since this difference can scarcely have any quantum-mechanical analog, it is concluded that a classical treatment cannot be satisfactory.

A PURELY classical calculation of the mean life of molecules formed by a bimolecular association reaction has recently been proposed by Kimball.[1] This treatment takes as the criterion for dissociation to have occurred the possession of a critical energy, D, by some natural coordinate of the molecule. The initial conditions chosen as corresponding to the formation of the molecule are potential energy $D+kT$ and kinetic energy zero for the natural coordinate involved in the dissociation, and both kinetic and potential energy zero for all other natural coordinates. The amplitudes of the motions in the various normal coordinates are thereby determined. The probability of dissociation per vibration of some suitable normal coordinate is then taken as the probability that the dissociable natural coordinate will have potential energy at least D when the kinetic energy of the chosen normal coordinate is zero.

There can be little doubt that some modification of this treatment is needed to take account of energy initially present in the other natural coordinates. We shall first consider a direct extension of Kimball's treatment.

Let the transformation from natural coordinates, y, to normal coordinates, x, be

$$y_i=\sum_{k=1}^{n} a_{ik}x_k, \tag{1}$$

where
$$|a_{ik}|=\begin{vmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ a_{n1} & a_{n2} & \cdots & a_{nn} \end{vmatrix}=1. \tag{2}$$

Then the transformation from normal to natural coordinates is

$$x_i=\sum_{k=1}^{n} A_{ki}y_k, \tag{3}$$

where A_{ki} is the minor of $|a_{ik}|$ associated with a_{ki}. The following relations are then fulfilled.

$$\begin{aligned} &\sum_{i=1}^{n} a_{ki}A_{ki}=1, \\ &\sum_{k=1}^{n} a_{ki}A_{ki}=1, \\ &\sum_{i=1}^{n} a_{mi}A_{ki}=0 \text{ when } k\neq m, \\ &\sum_{k=1}^{n} a_{km}A_{ki}=0 \text{ when } i\neq m. \end{aligned} \tag{4}$$

[1] G. E. Kimball, J. Chem. Phys. 5, 310 (1937).

The equations of motion in the normal coordinates are

$$y_i = y_{i0} \cos (2\pi\nu_i t + \epsilon_i). \quad (5)$$

Then at $t=0$ we have

$$y_{i0} \cos \epsilon_i = \sum_{k=1}^{n} a_{ik} x_{k0},$$

$$-y_{10} \sin \epsilon_i = \sum_{k=1}^{n} a_{ik} \dot{x}_{k0}/2\pi\nu_i, \quad (6)$$

where x_{k0} and $\dot{x}_{k0}$ are the initial values of the x_k and $\dot{x}_k$. The amplitudes of the motions in normal coordinates are therefore

$$y_{i0} = \{[\sum_{k=1}^{n} a_{ik} x_{k0}]^2 + [\sum_{k=1}^{n} a_{ik} \dot{x}_{k0}/2\pi\nu_i]^2\}^{\frac{1}{2}}. \quad (7)$$

An explicit expression for the ϵ_i is not needed.

The natural coordinates at any later time are then given by

$$x_i = \sum_{j=1}^{n} A_{ji} \{[\sum_{k=1}^{n} a_{jk} x_{k0}]^2 + [\sum_{k=1}^{n} a_{jk} \dot{x}_{k0}/2\pi\nu_j]^2\}^{\frac{1}{2}} \times \cos (2\pi\nu_j t + \epsilon_j). \quad (8)$$

We obtain a form more appropriate to the initial conditions by replacing x_{10} with $(D+x_{10}^2)^{\frac{1}{2}}$, so that x_{10}^2 now represents the initial potential energy of the dissociable coordinate in excess of the minimum energy D. Then when D is sufficiently large compared to the remaining energy in all coordinates we obtain by permissible approximations the following result, valid only for $x_1^2 \geqq D$,

$$\begin{aligned} x_1 &= \sum_{j=1}^{n} A_{j1} a_{j1} D^{\frac{1}{2}} \{[(1+x_{10}^2/D)^{\frac{1}{2}} \\ &\quad + \sum_{k=2}^{n} (a_{jk}/a_{j1})(x_{k0}/D^{\frac{1}{2}})]^2 \\ &\quad + [\sum_{k=1}^{n} (a_{jk}/a_{j1})(\dot{x}_{k0}/2\pi\nu_j D^{\frac{1}{2}})]^2\}^{\frac{1}{2}} \cos (2\pi\nu_j t + \epsilon_j) \\ &= \sum_{j=1}^{n} A_{j1} a_{j1} D^{\frac{1}{2}} \{1 + \sum_{k=2}^{n} (a_{jk}/a_{j1}) \\ &\quad \times (x_{k0}/D^{\frac{1}{2}})(1+x_{10}^2/D)^{\frac{1}{2}} + x_{10}^2/2D \\ &\quad + (\tfrac{1}{2}) \sum_{k=1}^{n} (a_{jk}/a_{j1})(\dot{x}_{k0}/2\pi\nu_j D^{\frac{1}{2}})]^2\} \{1 - \lambda_j^2/2\}, \end{aligned} \quad (9)$$

where λ_j are the phase angles of the normal vibrations at time t, and are all small, since the total kinetic energy must be small. The term

$$\sum_{j=1}^{n} \sum_{k=2}^{n} A_{j1} a_{jk} x_{k0}$$

vanishes identically, as is seen by reversing the order of summation. The condition that $x_1^2 \geqq D$ is therefore

$$x_{10}^2 + \sum_{j=1}^{n} [(A_{j1}/a_{j1})(\sum_{k=1}^{n} a_{jk} \dot{x}_{k0}/2\pi\nu_j)^2] \geqq D \sum_{j=1}^{n} A_{j1} a_{j1} \lambda_j^2. \quad (10)$$

This result differs from that of Kimball by the presence of the second term on the left of the inequality, which is approximately equal to the kinetic energy initially present in all the natural coordinates. The mean value of all the terms on the left is approximately $(n+1)kT/2$. The chance that (10) will be fulfilled when $\lambda_1 = 0$ is therefore

$$\frac{\prod_{j=2}^{n} A_{j1} a_{j1} [(n+1)kT/2D]^{(n-1)/2}}{2^{n-1}\pi^{(n-1)/2}\Gamma(n/2)}$$

or $[(n+1)/2]^{(n-1)/2}$ times the chance calculated by Kimball. This change means a very considerable reduction in the mean life for molecules of moderate complexity. Thus for the reaction

$$2NO_2 = N_2O_4,$$

$n=11$ and Kimball's value for the mean life must be divided by $6^5 = 8000$. For

$$H + C_2H_5 = C_2H_6,$$

the corresponding factor is $7^6 = 120{,}000$. The corrected mean lives, 6×10^{-10} sec. and 2×10^{-5} sec., respectively, are still as great as there seems any experimental need for.

It is questionable whether a calculation of this sort has much significance. In the first place, it has neglected the ordinary restrictions of classical quantum theory. One effect of these restrictions, of course, would be to reduce the average kinetic energy of the natural coordinates. This restriction applies, however, to the entire class of collisions, not necessarily to the infinitesimal fraction of that class permitted to form molecules. Thus one might plausibly argue that the introduction of

quantum restrictions must be expected to favor the dissociated states, and therefore that the classically calculated mean lives will certainly be longer than those based on quantum theory. The whole machinery of the old quantum theory is so unsuited to problems of this sort, however, that it does not even furnish language in which they can be discussed intelligently.

A quantum-mechanical theory must give an essentially different result from that of the classical treatment, since it is meaningless to specify both the phases and the energies of the various normal vibrations. The radically different roles played by kinetic and potential energy in the classical theory must somehow be merged. It appears, therefore, that we are forced back to the quantum-mechanical theory Kimball's treatment had attempted to avoid.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

The Raman Spectra of Deuterated Benzenes and the Symmetry of the Benzene Molecule

In connection with a study of the structure of the benzene molecule, we have prepared all of the deuterium-substituted benzenes and have obtained their Raman spectra. The preparative and spectroscopic details of this work will be published shortly. We desire, however, to call attention to a striking feature of the Raman spectra of these compounds which offers constructive evidence of the D_{6h} (plane hexagonal) structure of benzene.

It is well known[1] that there are in benzene two fundamental frequencies which have very nearly the same value, *viz.*, the totally symmetric frequency (ν_1) of 992 cm^{-1} and the trigonally symmetric frequency (ν_{12}) at about 1010 cm^{-1}. The latter vibration is, by reason of its symmetry, forbidden in Raman effect. The reduced symmetry of the deuterated benzenes, however, evokes its appearance in the Raman spectra of all these save the *para* di- and the *para* tetra-substituted compounds.

For practical reasons one cannot compute in a rigorous fashion the shifts of these two frequencies caused by the insertion of deuterium atoms in the benzene molecule. On the other hand it is possible to estimate the shifts closely enough for our purposes by making the plausible assumption that a constant frequency decrement results from the substitution of each deuterium atom. The decrements in ν_1 were found simply by dividing the benzene- hexadeuterobenzene shift by six. Since ν_{12} is inactive in both compounds, a similar procedure for this frequency is impossible. We have therefore estimated the various ν_{12} values as follows: The calculated ν_1 values agree quite closely (within *ca.* 1 cm^{-1}) with observation in the *ortho* and *para* di- and tetra-substituted compounds. Presumably the assumption under which the several ν_1 frequencies were calculated would therefore be equally valid for these same compounds in calculating ν_{12}. This frequency is inactive in the *para* compounds, but from the observable *ortho* frequencies one can compute the shift in ν_{12} for each additional deuterium atom. From this information ν_{12} has been estimated for the various deuterated benzenes.

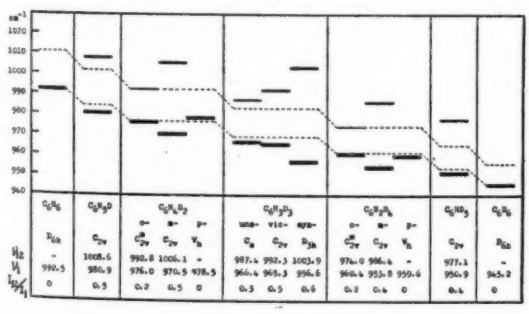

FIG. 1.

In Fig. 1 the dotted lines show diagrammatically the calculated shifts in ν_1 and ν_{12}. Our method of calculation of course gives the same value for a given frequency within each group of isomers. The frequencies of ν_1 and ν_{12} observed by us in the Raman spectra of the deuterated benzenes are listed in the table at the foot of Fig. 1, together with the symbols for the symmetry classes of the respective compounds. It is important to remark that in all of the deuterated benzenes with symmetry C_{2v}, except the *ortho* di- and *ortho* tetra-substituted compounds, the vibration ν_{12} is symmetric to the twofold axis. In the *ortho* compounds, however, the twofold axis passes between the two *ortho* carbon atoms, and ν_{12} is thus antisymmetric to the axis. To emphasize this distinction, we have marked the *ortho* compounds C_{2v}*. ν_1 is of course a totally symmetric vibration in *all* the compounds. For convenience in comparison with the calculated values, the observed frequencies have been inserted in Fig. 1. The visually estimated intensity ratios of ν_{12} to ν_1 are given in the column I_{12}/I_1 and approximately indicated by the thickness of the plotted levels.

When one examines Fig. 1, one is struck by the fact that in certain of the compounds, the frequency ν_1 is *lower* than the calculated value by several wave numbers, and that ν_{12} is *higher* than calculated by about the same amount. *This unexpectedly large separation of ν_1 and ν_{12} occurs only in those compounds in which the corresponding normal modes of vibration belong to the same symmetry class.* It is further to be remarked that whenever an increased separation is found, the intensity of ν_{12} is enhanced, *and the intensity increase is the larger, the larger the separation.*

It is difficult to see how these features of frequency and intensity can be explained on the usual mechanical grounds and in accordance with the well-established theoretical principles of the Raman effect unless one assumes the

D_{6h} structure. Once this assumption has been made, however, the explanation is simple and complete. The discrepancies between calculated and experimental frequencies, and the attendant intensity differences, are due to resonance between ν_1 and ν_{12}. This resonance can occur only in C_s, C_{2v} (but *not* C_{2v}*), and D_{3h}, and it is *only* in these cases that we find anomalous frequencies and intensities.

We therefore believe that these particular features of the Raman spectra of the deuterated benzenes strongly support the D_{6h} structure.

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